Journal Of Applied Chemistry

Vol. 24 No. 11

THE GREATEST CONSTRUCTIONS OF THE STALIN EPOCH AND THE MATERIALS FOR BUILDING THEM

P. P. Budnikov

The Government of the USSR has taken the historic decision to construct, on the banks of the great Russian river Volga, the Kuibishev and the Stalingrad hydroelectric power stations, the Grand Turkmen Amu Darya Krasnovodsk canal, the Kakhovka hydroelectric station on the banks of the river Dnieper, the South Ukrainean and the North Crimean canals[1], the Volga-Don navigable canal, and to irrigate the soil of the Rostov and Stalingrad districts[2].

The Kuibishev and Stalingrad power stations will, within 5-6 years, produce some 20 milliards of kilowatt hours in a year of average rainfall. The output of each of these stations will exceed by several times that of the Lenin Dnieper station, and will surpass the output of all known stations throughout the world. The construction of these hydroelectric stations will permit the irrigation and watering of about 14 million hectares of soil in the regions of the lower Volga and the Caspian sea, and will permanently free their agriculture from drought and aridity; at the same time it will raise the productivity of the soil of the lower Volga region. In this way the possibility will be created for exploiting still more completely the inexhaustible natural resources of the Volga region, for extending the production of Zhigulev petroleum, for ensuring the greater development of various branches of industry and transport, and for introducing advanced technique into existing industries.

The construction of the Grand Turkmen canal from the Amu Darya to Krasnovodsk, with a length of 1100 km, irrigating and watering the northern region of the Caspian plain, western Turkmenia, the lowlands of the Amu Darya and the western part of the Kara-kum desert, opens up wide horizons for the further development of the productive capacities of the Central Asian republics, including the Karakalpak Autonomous Socialist Soviet Republic. The plan for the transformation of the Kara-kum desert envisages irrigating, and establishing an agricultural basis in 1-3 million hectares of waterless land, mainly for cotton production. The realization of the construction of the Grand Turkmen Canal will resolve the great problem of developing the territory of the Kara-kum. The irrigation and

---

[1]) The decree of the Council of Ministers of the USSR for the construction of the hydroelectric station was published on August 21, 1950; for the construction of the Stalingrad power station on August 31, 1950, for the construction of the Main Turkmen Canal Amu Darya-Krasnovodsk on September 12, 1950. On September 21, 1950 the decree was passed for the construction of the Kakhovka power station on the Dnieper, of the South Ukrainian and North Crimean canals, and for the irrigation of the soil of South Ukraine and North Crimea.

[2]) Decree of the Council of Ministers of the USSR, December 28, 1950.

watering of millions of hectares of this desert region will enable the production of cotton to be increased many fold; it will permit the establishment of livestock production, of sericulture, and of various agricultural crops.

The waters of the Amu-Darya will cause a new jump in the development of the industry of Krasnovodsk, Nebitdaria, Kara-Bogaz-Gol and of Cheleken. The canals will enlarge the waters on a grand scale, uniting the far regions of Central Asia, through the Caspian Sea and the Volga, with the Central regions of the USSR.

The construction of the Kuibishev and Stalingrad hydroelectric stations will create enormous water reserves. The jump in the level of waters, as a result of the damming and regulation of the flow from the reservoirs, will deepen the Volga in the middle and lower parts of its course. This will enable large vessels to ply on the Volga and the Kam.

According to the decree of the Council of Ministers of the USSR, in the region of the Kakhovka river the construction and opening of the hydroelectric station on the Dnieper should be completed in 1956, and in 1957 the construction of the South Ukrainian and the North Crimean canals should be finished, together with the project for the irrigation of the regions of the Southern Ukraine and Northern Crimea.

The Kakhovka hydroelectric station will be one of the largest sources of energy on the Dnieper, and will have a capacity of 250,000 kilowatts, with an output of 1.2 milliard kilowatt-hours per annum during a year of average rainfall.

The South Ukrainian canal, with an intake of water from the Dnieper of 600-650 m^3/sec., will proceed from Zaprozhe on the Dnieper to the river Molochna, then in the direction of Askania-Nova through Sivash, crossing the Southern Crimea canal in the Steppe region of the Crimea to the river Kerch. The total length of both canals will be 500 km.

On the river Molochna, to the North of Melitopol, it is planned to create a water reservoir of a 6 milliard cubic meter capacity and with a hydroelectric station with dams of 10,000 kw capacity. There will likewise be constructed small water reservoirs in the course of the canal with a total volume of not less than 1 milliard cubic meters.

For the Kakhovka hydroelectric station an enormous lake of 14 milliard cubic meter capacity will be created which will take waters from the Dnieper and increase the depth of the river Kakhovka up to the dams of the Lenin-Dnieper station. The Kakhovka hydro network, as well as solving problems of power and irrigation, will considerably facilitate the passage of vessels from the dams of the Dnieper power station to Kakhovka; the construction of a lock is projected for this purpose.

The hydroelectric station in the region of the river Kakhovka will ensure cheap electricity to the entire agricultural economy of the Yug region, creating a sound basis for electrification of agriculture. Powerful pumping stations are planned for feeding water to the fields in the region of Kakhovka. An important part of the electrical energy is earmarked for industrial and domestic needs.

The construction of the Kakhovka hydroelectric station and the irrigation system of the Southern Ukraine and the Northern Crimea will provide water for 3.2 million hectares of land which is at present arid, and which will thereby be converted to fruitful fields and pasture.

The building of the gigantic projects of the Stalin epoch on the Volga and in Central Asia, on the Dnieper, in the arid southern region of the Ukraine and in the Northern Crimea, the construction of the Volga-Don navigable canal and the

irrigation of the soil of the Rostov and Stalingrad regions, these will ensure a high and stable level of agriculture and a still larger development of our industrial potential. Gorki's vision – " to treat all our land as a garden, to provide water for the waterless deserts, to canalize and deepen the rivers, to construct millions of kilometers of new roads, to cleanse our enormous forests" – is now being unrolled before our eyes.

Achievement of the Stalin plan for gigantic constructions, to change the face of nature, to conquer sandy deserts and convert them to colorful fields, towns, and villages is possible only under the conditions of Socialist construction and planned economy, facilitated by the real flowering of our advanced Soviet science, that science which devotes its entire strength to our Motherland.

In order to assess the magnitude of the constructional work involved in the erection of the Kuibishev, Stalingrad, and Khakovka hydroelectric stations it is sufficient to quote only a few facts.

For the construction of the Kuibyshev power station 150 million cubic meters of earth must be raised (excavations, embankments, rock excavation; etc.). 6 million cubic meters of cement and ferroconcrete must be laid, for which 1,700,000 tons of cement will be required.

For the construction of the Stalingrad hydroelectric station 102 million cubic meters of earth have to be extracted, 6.5 million cubic meters of ferroconcrete must be poured, at a rate of not less than 1,000 cubic meters per day.

An enormous volume of work will be involved in the construction and assembling of equipment, metal construction, hydroelectric equipment, and various machines.

For the construction of the Kakhovka hydro-network, the volume of only some of the earthworks and canals is about 250 million cubic meters, and the laying of about 1.8 million cubic meters of concrete is required.

The construction of the Kuibishev and Stalingrad hydroelectric stations, of the Grand Turkmen Canal, of the Kakhovka hydroelectric station and of the Southern Ukrainian and Northern Crimean canals requires the use of new earth-moving techniques, mechanization, and automatic machines. In this construction work the newest Soviet mechanisms will be used – earth-movers of capacities up to 1000 m^3/hr, electrical excavators of capacity 200-300 – m^3/hour, scrapers, bulldozers, etc.

In the construction of the hydro-network, main roads and trunk line railway bridges will be laid across the river Volga.

Fulfillment of the complex plans of hydrotechnical construction, requires, in the first place, an enormous quantity of cement and of inert rock material as cement filler.

The extensive construction of permanent and temporary buildings, of industrial plants, warehouses, roads, approaches and houses likewise requires enormous quantities of building materials – cement, lime, plaster, bricks, and glass. Local and natural building materials take a prominent place. There are also required in enormous quantities various kinds of structural details, wall materials, heat insulating materials, reinforced concrete and reinforced silicate parts, asbestos-cement sheeting, facing materials, etc.

A rational form of construction of prefabricated buildings for living and social purposes should be worked out, and also of buildings for cultural assembly.

The quality of the cement is of extreme importance for these hydrotechnical projects. Millions of tons of high quality cement are required, with a specific

rate of setting, with low heat generation in setting and hardening, high mechanical strength, high modulus of elasticity, and minimum shrinkage; it must be frost and corrosion resistant, resistant to the effects of water, salt, and the atmosphere, resistant to wear and to the cavitation effects of flowing water, etc. A cement is required which will stand up to changes in loads and to vibration.

The setting delay, heat liberation in hydration, and the other physical and chemical properties of cement should be such as to permit the casting of packing blocks of more than 4000 cubic meters.

Since the hydro construction should have a long life, particularly stringent requirements must be fulfilled by the building materials. For this reason rapid methods of determining the quality and life of concrete and other structural materials should be worked out, and improved apparatus for the control of the working of hydrotechnical constructions during service should be developed.

The constructor of the Stalingrad station states that the principal scientific and practical problem there is the provision of means for consolidating soft ground.

The foundations for the basic constructions of the hydro network, the spillway dam, the header hydroelectric station, and the lock, should be ready for laying concrete in 1952. The excavations are extremely large, about 2.5 x 1.2 km, the depth below the water level being more than 25 m, for which enormous spillways are required. Apart from this, it will be necessary to have cheap means of strengthening the soft ground at the perimeter of the foundations and in the excavations; such strengthening is required for diminishing the inflow of water, for diminishing the volume of earth removed under the structures by greater slopes of the ground, and to diminish the depth removed by an artificial change in the ground in the foundations.

One of the principal and primary questions is that of ensuring the quality of the cement and the concrete, and likewise that of the inert fillers. The selection of the cement should be based upon the attendant conditions in the various zones of the hydrotechnical constructions; a scientific basis is required for the mineralogical composition of the clinker, the type of cement, the specifications for resistance to sulfate and carbonate attack, and to expansion, etc.

For a guaranteed construction a cement of at least mark" 500" is required, containing not more than 5-6% of tricalcium aluminate, and an enhanced calcium silicate content. The question of hydraulic additions to cement for the concrete casing of slabs, 2.5 x 4-5 m with a thickness of 8 cm, subsequently steamed, requires study, because these slabs are subject to particularly severe tests in service in the most active zones. It must not be lost sight of that this problem may be solved by additions of organic surface-active materials to the cement.

It is necessary to decide what cement should be used for under-water concrete and for casings. It is possible that the sandy pozzuolanic cement, as has been shown by the collective work of our scientists (Shestoperov, Kuvykin, Yung, Butt, Royak and others) is very strong, has low heat release, low shrinkage, high anti-corrosion and other technical properties. In this cement the maximum use is made of the chemical energy of the clinker by an optimum chemical and mineralogical composition, by fine grinding, and by accelerating the hydration by hydraulic additions and grains of quartz in the cement. In this way a cement has been developed which answers the specific requirements of the hydrotechnical constructions and is distinguished by a high economy in production and use.

The sandy-pozzuolanic cement contains 40-60 % of local raw materials. The hydraulic additions (for example -tripoli) can be introduced in the concrete mixer in the form of a milky suspension in water, (wet pozzuolanization, proposed by

Shestoperov and Kubykin) and does not require expenditure of energy in grinding. The problem of using these cements in the new constructions requires study, with special emphasis on their behavior during the ten years since the erection of the hydro-constructions referred to.

One of the problems which requires solution is that of protecting concrete from attack by carbon dioxide. The seriousness of the attack of CO_2 on cement requires study in the regions where these constructions are being made – Kuibishev, Stalingrad and Kakhovka: measures for protecting concrete (under varying conditions such as concentration of CO_2 and salts, temperature, rate of filtration of the substance through the cement, density of the concrete, etc.).

In the construction of the Kakhovka power station, the probability of attack of the cement by magnesium and sodium sulfates and chlorides, and also by gypsum dissolved in the water, must be reckoned with. Belite cement will possibly find application here. The mineralogical composition of the clinker part of this cement should be such that the ratio of the tricalcium silicate (alite) to dicalcium silicate (belite) is less than unity. The tricalcium aluminate content should be not more than 6-7%. It is a good idea to add to this cement 15% of granulated basic slag, tripoli or trass, as the investigations of Gershman (Cement Institute) have shown.

During hardening, the cement (as a result of colloid formation) suffers more or less shrinkage on drying, depending on its mineral composition. In a number of cases as, for example, the finishing of the internal surfaces and tubing of water conduits, a non-shrinking cement is required. But for sealing the joints between concrete slab casings and for building up sectional ferro-concrete into a monolith, it will possibly be necessary to use the widely publicized water-impermeable cement.

In order to eliminate filtration of water through highly porous ferroconcrete tubes exterior layers of gunite are formed (12-13 mm thick).

The use of such cements (guniting method) in the construction of subterranean and underwater structures enables them to be made water-proof. Treatment of water conduits with such cements renders them impermeable.

Among the methods proposed for the production of cement, that worked out by us at the Chemical Technology Institute of D. I. Mendeleev together with the Moscow Institute of Cement is of most practical interest. This method of manufacturing cement is distinguished by a considerable simplicity, and does not require aluminous cement: dolomite, roasted at 700-900°, is added to Portland cement during grinding. The process of expansion continues until all the magnesium oxide in the dolomite is completely hydrated. For water storage samples, (mortar 1:0) the expansion during a day is 0.2-0.6%, for mortars 1:1.5 it is 0.1-0.3%. The expansion of the cement depends on the temperature of roasting of the dolomite and the mineral composition of the clinker.

Owing to the need for the rapid erection of concrete structures and for putting them into service in the shortest possible time, AG cement has considerable importance [1]. This cement is prepared for the construction of concrete industrial and municipal buildings in grades having different moduli, for the rapid construction of reliable massive concrete structures which can be put into service 1-3 days after the completion of pouring. It can be used successfully for the rapid construction of bridge supports, thick supporting walls (thickness above 0.7 m), massive concrete foundations, etc.

In view of the good stability of concrete made from AG cement against water containing a considerable amount of salts (particularly NaCl, Na_2SO_4 $MgSO_4$), it may be used with success for the rapid construction of massive port installations (breakwaters, piers, embankments). Its use is also effective for a number of cases of hydrotechnical construction in fresh water, owing to its extremely small shrinkage, its water impermeability, high strength, etc. [2].

The ultimate compressive strength of AG cement (mortar 1:3) under adiabatic conditions at 50-60° is 400-500 after one day and 500-600 kg/cm$_2$ after three days, while its tensile strength is 24-27 after one day, and 27-30 kg/cm$_2$ after three days. The maximum possible strength of concrete from AG cement is 900 kg/cm^2.

AG cement shrinks several times less (0.0006%) in hardening under atmospheric conditions, than do aluminous and Portland cements, for which the period of shrinking ends after 3-4 days. In water AG cement behaves as a non-shrinking cement, which makes it usable for the jointing of restored concrete and ferroconcrete structures into monoliths.

In spite of the relatively rapid start in the setting of the cement (20-30 minutes), concretes from AG cement maintain their fluidity and pourability for up to an hour after the start of setting. The strength of the cement laid one hour after mixing is not less than that cast immediately after mixing.

AG cement gives pastes less viscous than those of any other cement, so that it can be used for the preparation of highly mobile concrete with the least expenditure of cement.

The consumption of cement for the minimum normal thickness of concrete, all other conditions being the same, is the smallest. The consumption of AG cement per cubic meters of concrete is 8-15% less than that of Portland cement.

In order to utilize the potentialities of the cement to the best advantage, Shestoperov proposed to wet-grind the clinker or eliminate grinding by introducing peptizing and plasticizing agents and an amount of gypsum in excess of that laid down by the State Standard Organization.

The organization of wet-grinding of clinker or of fine-grinding of the cement should be bound up with the preparation of mortars and of concretes at specially organized constructional combines.

Practice shows that certain surface-active agents can effect a great saving of cement, improve the workability of the concrete mix, and the control of the setting time of the cement; lower the heat liberated by, and the hydration of, the cement in the initial stages of hardening; and they can improve its structural and mechanical properties, its water impermeability and salt resistance.

The physico-chemical basis for the action of surface-active agents on concrete has been worked out by Academician Rebinder. According to him, surface-active materials can be divided into hydrophobic and hydrophilic; they differ sharply from one another in their action on cement.

According to investigations of Stolnikov [3], hydrophobic materials have froth forming properties which are reinforced by $Ca(OH)_2$, always present in the water of the concrete mix as a result of the hydration and hydrolysis of cement, and forming on the surface of bubbles of emulsion envelopes of solid, fairly finely divided calcium soap.

The introduction of such air-entraining additions into the concrete mix in quantities of 0.08%, according to Stolnikov, causes some lowering of its strength but, on the other hand, induces a considerable lowering of the water:cement ratio of concrete mixtures, giving them the shrinkage required for underwater use. Air-entraining additions permit a considerable lowering of the friction between the concrete mix and the walls of tubes, and for this reason are beneficial when pumping concrete mixes.

Hydrophilic surface-active agents are added to cement as peptizers. Added to cement paste in very small quantity (0.1-0.3%) they change its degree of dispersion,

subdivide (deflocculate) aggregated cement particles into primary particles, and at the same time considerably raise the mobility of the cement. Adsorbed on the surface of the cement particles, these agents exert a considerable effect on the kinetics of the hydrolysis and hydration of the cement paste in mortars and concretes, on the setting and hardening of cement, and on the physical and mechanical properties of concrete.

Surface-active agents are of considerable value for raising the mobility of mortars and concretes, for raising the strength and increasing the economy of cement, its frost resistance, water impermeability, and for increasing its deformability.

However, as investigations by Shestoperov (Institute of Highway Construction) have shown, the effect of surface-active additions depends on their concentration, the fineness of grinding of the cement, the mineral composition of the clinker, and also on the quantity and modification of the gypsum (dihydrate, semihydrate, or anhydrite). This has been confirmed by other investigators. From work carried out at the Institute of Highway Construction, it follows that in some cases surface-active agents raise the strength of mortars and concretes, and in other cases, the increase in strength in practice is extremely small, and finally, in certain cases the use of additions causes the setting of cement to accelerate.

In order to confirm our ideas about the effects of surface active additions on various technical properties of cements, mortars and concretes, further investigation is necessary.

The use of surface-active agents is closely connected with the question of the durability of mortars and concretes when exposed to successive freezing and thawing, and to media of different aggressiveness.

The possibility of using local ground and lake waters for the preparation of mortars and concretes needs study.

In hot climates, where special difficulties are met with in relation to water, it is necessary to protect the cement, during hardening, from rapid evaporation and, in order not to disturb the process of hardening cement, the concrete revetments of canals must be covered with a special emulsion.

An important problem is the development of a cheap method of treating the surfaces of irrigation canals to prevent the spread of plant growths on them.

The construction of power stations requires enormous quantities of inert minerals, and poses special questions such as: the possibility of using, for example, non-frost resisting carbonates (burnt dolomitic limestone) as a filler in zones of frost resisting concrete, and likewise for paving the slopes of canals and of earth dams (Mogutov mountain, Soks mountains, Shiryaev dolomite beds [4]). For overwater constructions large quantities of sandy, granitic, prophyritic, and other natural diabase rocks are required.

Not less important is the question of the effective utilization of fine-grained sands in concretes, for example, sands of the Southern Crimea, Karakum etc.

The construction of the Stalingrad hydroelectric station emphasizes the need to work out a cheap method of obtaining stone from sand, at least for constructing bankets of alluvial dams, for the paving of slopes and highways without stone. The requirements of stone for these purposes alone runs into several millions of cubic meters. Rubble for concrete and rough stone for foundations need to be transported distances of 300-600 km, which makes the construction very much more expensive. In the immediate neighborhood of the constructional area there are large deposits of quartz sand.

It is necessary to work out a reliable method of consolidating shifting sands.

The hydroelectric stations in the Volga and Dnieper are constructions of the great Stalin Epoch, the epoch of the building up of communism, and hence the architectural form of the structures should be beautiful and functional. For the external facing of the Volga power station and other permanent structures natural Ural stone may be used, which will ensure a durable building; for the interior and finishings of the structures and buildings ceramic parts should be employed.

The Ukraine and the Crimea are rich in mineral deposits which can be widely used as walling and decorative facing materials: sawn limestone, coloured marble-like limestone, granite, diorite, labradorite and many others [5]. All of them can be used as durable structural materials for the construction of the Kakhov hydroelectric station, of various industries, permanent buildings, living quarters, etc.

For the construction of hydroelectric stations and canals, apart from high quality cement which will ensure a durable structure, and natural decorative stones, enormous quantities of structural materials for the erection of permanent buildings, industrial plants, warehouses, dwelling houses, etc., are required.

Local constructional materials ought to be of great practical importance for industrial, domestic, and other structures. Among such materials should be numbered slag cement, slag concrete structural parts, gypsum bonding (structural and high strength gypsum, anhydrite cement, trimmed gypsum, water resistant gypsum, [6]), and heat insulating materials (foamed concrete silicate, and microporite, etc).

Many years of practical testing of the clinkerless slag cement proposed by us has shown that it is of high quality. With the proper organization of its production, it is possible to produce this cement, of mark " 250-300" and higher [7]. By wet milling blast-furnace slag with the additions used for clinkerless cement, a cement of mark 500 and higher may be obtained, as investigations by Yung and Butt have shown. Clinkerless slag cement is noted for its chemical stability in water containing dissolved sulfates, for the low heat liberation during hardening, which puts it well above other cements. Thus, while the heat generation by clinkerless slag cement is 15-26 cal/hr during 7 days hardening, the activity of the cement being 200-350, the heat liberation by Portland cement, with an activity of 350-400 during the same interval of time is 55-75 cal/hr.

The direct production of constructional mortars and concretes on the site, and the organization of the large scale production of slag concrete constructional parts using local raw materials, makes it possible to economize very considerably on the transport of cement from other regions, of inert materials and of fuel. In particular, there should be a wide utilization of local bonding materials, particularly of concrete and mortars on the basis of boiler slag, slaty ash and burnt ore, which are wastes of the coal, transport, metallurgical, and steam raising industries, etc. The method proposed by Maximovsky [8] for the treatment of these raw materials can be accelerated by other means. Instead of mortar mixers the author favors edge-runner mills. Fuel slag, enriched by sifting out the unburnt fuel and fine particles of ash is ground dry in an edge runner mill for 1-2 minutes together with cement. After this, the intimate mixture of slag and cement is wet-ground in the same way, 3-5 minutes, for which purpose an aqueous suspension of lime is added. In this way a wallstone is prepared, suitable for ceilings between stories, for partition slabs, and other elements of sectional buildings; the saving of cement is 50-70%. The ultimate compressive strength of articles one day after preparation is from 70-150 kg/cm^2.

Wide use should be found in the constructional details of different industrial and domestic buildings, for such light materials as: cellular concrete, made from cement, lime, clay, and different fillers (slag, marshallite, sand, slate, ash,

tripoli, waste ashes, etc). Foamed concrete, foamed silicate, aerated concrete, microporite, foamed glass, foamed slag, etc, will be of great practical value.

Kudryashov proposed the use of autoclave slabs of reinforced foamed concrete and reinforced foamed silicates, the density of which is from 600 to 800 kg/cm^3. Foamed concrete differs from foamed silicate in that the latter contains ground lime (quick lime) instead of Portland cement. Such slabs, apart from their non-functional uses, act as thermal insulators and diminish the weight of covering to 80-100 kg/cm^2 from the 300-350 kg/cm^2 for ferroconcrete with a thermally insulating layer.

Gulinova, Kornilovich, and others (Institute of Constructional Materials of the Architectural Academy of the Ukrainian USSR) worked out a method for preparing new forms of constructional and heat insulating materials from local raw materials—the so-called "structural microporite". The method of manufacturing this material is simple and consists in grinding together clay, lime and sand with a large quantity of water, introducing into the slime obtained a solution of water glass as a stabilizer, and subsequently autoclaving and drying the prepared article. Microporite, according to data of the authors mentioned, can be obtained with a volumetric weight of 0.3-0.9 kg/m^3, and with an ultimate compressive strength of 15-110 kg/cm^3. The thermal conductivity is 0.1-0.2 k cal/m/hr/°C. Such a material, along with foamed silicate, can find wide application in construction, particularly as a thermal insulating slab for house construction, and also as a sound and heat insulating covering. When using microporite as an exterior wall for buildings of low story height, it must be faced with bricks, ceramic slabs or other materials.

The new thermal insulating material "foamed glass" should find wide application; it was proposed by Kitaigorodsky. This is a handsome insulating material prepared in the form of blocks and slabs from powdered glass by sintering it with a gas producing material, with later thermal and mechanical treatment.

The volumetric weight of foamed glass is 200-300 kg/m^3, its compressive strength is 30-50 kg/cm^3, and its bend strength 7-10 kg/cm^3. The material can easily be sawn, has a very small moisture absorption and a good coefficient of sound absorption; it can also be used for the construction of enclosed buildings and for the thermal insulation of different heating and cooling installations.

The use of thermal insulating materials not only enables the consumption of basic building materials to be reduced, but also facilitates the industrialization of the production of constructional works. Thermal insulation is necessary for enclosed constructional buildings, heat generating stations, conduits, electric power stations, plants, etc.

Among the various insulating materials, sintered ceramic parts can be used; they are prepared from tripoli and diatomaceous earth, in the form of bricks, shells, and segments by including in their initial composition materials which can be burned out; foamed tripoli can also be used. The volumetric weight of these articles varies between 500 and 800 kg/m^3. Mineral wool (slag wool), prepared from melts of rocks and slags, should find application, especially in the form of finished articles made from it. It is important to use for this not only the untreated raw wool, but also soft rolls- mineral felt and matting; hard articles - slabs, shells and segments; friable materials- granulated wool and insulating cement made from it, and used as a mastic.

The volumetric weight of mineral wool covers a wide range - 150-350 kg/m^3 and even 30-50 kg/m^3.

Considerable use may be found for molded asbestos cement insulating blocks,

prepared from a mixture of disintegrated asbestos and cement. These articles make excellent insulating roofs of industrial buildings, heating systems and industrial installations.

Apart from the usual constructional bricks of clay and silicates, wide use should be found for hollow and porous bricks, and also for hollow ceramic blocks and a number of other constructional materials. In extending the production of building bricks, wide use should be made of the method worked out by Stakhanovite Duvanov [10] , literally overthrowing all existing norms of production of baking furnaces. Duvanov created a completely new method of baking bricks, raising the productivity of furnaces to 2500 and more bricks per m^3 of the furnace space. The high output of the ring shaped furnaces was attained by lowering the density of packing (and the system of stacking) the raw bricks in the furnace from 250 to 185-190 units per 1 m^3 of the furnace canal; thanks to this lowering of the resistance of the brick stack (direct stacking, i.e. end to end) the rate of movement of the fire through the stack has been considerably raised.

The exceptional value of the rapid method of roasting bricks consists in the fact that its wide application in the brick industry scarcely requires any capital expenditure. It is important in this procedure to eliminate the interruption between the drying of the raw bricks and the actual baking.

Among other things, Dubanov posed various questions concerning the thermal economy of the drying of raw bricks, and its intensification.

Wide use in building should be found for a new form of constructional brick - the clay-lime autoclaved brick. This was first obtained by us under laboratory conditions in the Kharkov Institute of Chemical Technology, and afterwards in a silicate plant in 1927 [11].

The raw bricks, formed from a dry mixture of clay with 7-8% of lime, (to the lime may be added tripoli, blast furnace slag, sand, marl, volcanic ash, ash, and so on) with a strength of 36-50 kg/cm^2, are subjected to steaming under a pressure of 7-8 atm for around 6-8 hours, depending on the kind of clay. The ultimate compressive strength of the prepared clay-lime autoclaved bricks is 125-135 kg/cm^2. In the course of time, as our investigation and work of Yakovlev and others (Institute of Local Constructional Materials, MPSM, RSFSR) showed, the strength of clay-lime bricks increases during one year to 190 kg/cm^2. Clay-lime autoclaved bricks, prepared under plant conditions, have an ultimate compressive strength of 130 kg/cm^2, and a bend strength of 30 kg/cm^2, with a water absorption of 11-13.5%. The ultimate compressive strength after a 15-fold freezing treatment is 95 kg/cm^2. The thermal conductivity varies between 0.694 and 0.858 k cal/m,hr. i.e. is practically the same as that of silicate bricks.

Since the production of clay-lime silicate bricks can be mechanized (use of presses and moving of bricks on wagonettes), and the consumption of lime and fuel can be reduced, its production cost should not be higher than that of silicate lime-sand bricks and considerably less than that of the usual clay bricks in the plastic and dry forming process. Apart from this, the enhanced strength of the bricks permits the production of hollow blocks and of facing slabs. While the duration of the production cycle for the usual building brick, following the plastic method, is 10-15 days, and that of the so-called " dry method" of molding is 6-8 days, the production of a clay-lime brick by the autoclave method only takes 10-12 hours altogether. The hardness of these latter bricks is obtained by the hydrocalcium silicates and aluminates.

The electrical energy of the Kuibishev and Stalingrad, and also of the Kakhovka power station, will be fed into some grid lines at a transmission voltage of 400 kV.

The electrical energy at this voltage will be transformed at sub stations and distributed to the consumers thrdugh the local networks at 220 and 110 volts. This will require enormous quantities of large dimension porcelain insulators.

Hence new technical, constructional, and organizational problems will face the ceramic industry concerned with the production of electrical insulators.

For line transmission at 400 kV the question arises as to whether porcelain is suitable for the construction of large size insulators, or whether a new heat-stable ceramic material is required, having a high mechanical strength and dielectrical properties, exceeding for instance by 25% the performance of present day insulators, and this in turn will require new kinds of raw material.

Thus the problems of seeking out new glazes or coatings, of improving the wet discharge potential, searching for new cements and armorings, arise. The need for increased production of certain forms of ceramic insulator by a factor of 8-9 raised the problems of intensifying the process (mechanization, accelerating the casting, drying, and polishing).

When investigating porcelain as a material for the construction of large size insulators, it is important to remember that it is not only used as a dielectric, but is subjected to dynamic loads as well.

The enormous amount of electrical energy which will be poured out from the power stations will stimulate the development of different branches of industry, particularly the electrochemical and chemical industries. Thus the construction of the Kakhovka station on the Dnieper, the southern Ukrainian and Northern Crimean canals and the irrigation of the soil of the southern Ukraine and Northern Crimea, will create favorable conditions for the development of chemical industry, for the complete utilization of the rich raw materials of the Sivash and the Perekop group of lakes. The latter a long time ago attracted the attention of our specialists. These lakes constitute an inexhaustible source of different kinds of salts and slimy deposits, and so are rich sources of raw materials for the chemical and building industries and also for balneology.

The bond between Soviet science and the motherland plays in practice an enormous part in its development and growth. The creation of power stations on the Dnieper and the Volga, and the irrigational works will provoke a new vigorous upsurge and a still greater growth of Soviet science in the different fields of knowledge, culture, and art. The great Stalin construction, this newly appearing, unalterable friendship and brotherhood in the Soviet motherland, are evidence of the strength, power and superiority of the Soviet Union over the capitalist countries. At the time when the USA and the other capitalist countries are seeking nothing but for the feverish pursuit of armaments, leading to a war for plunder, barbarously destroying the peaceful population of towns and villages of Korea, the Soviet Union, in spite of the international tension, maintains before its eyes its unchanged peace-loving policies, and carries on creative constructional work, building the largest structures in the world, changing the face of nature and subjecting it to the control of man in the name of the well-being and the prosperity of the Soviet motherland, and in the name of the victory of communism.

LITERATURE CITED

[1] P. P. Budnikov and G. G. Goldenberg, Proc. Acad. Sci. USSR, 3-4, 73-84 (1942).

[2] P. P. Budnikov and G. G. Goldenberg, J. Appl. Chem. 18, 1-2, 15 (1945).

[3] V. V. Stolnikov, Proc. Acad. Sci. USSR 72, 2, 331 (1950); S. V. Shestoperov,

T. Yu. Lubimova and F. M. Ivanova, Proc. Acad. Sci. USSR 70, 6, 1045 (1950); Yu. M. Butt and T. M. Berkovich, Proc. Acad. Sci. USSR, 55 (1949); A. V. Satalkin and M. B. Kublanova, Proc. Acad. Sci. USSR, 72, 3, 561 (1950).

[4] O. K. Yanatyeva, Bull. Sec. Phys. Chem. Anal., Acad. Sci. USSR, 20, 252-268 (1950).

[5] O. O. Litvinov and I. S. Soloninko, Granite, Labradorite, and Marble, Pub. by Acad. Archit. Ukrainian SSR, Kiev, (1950).

[6] P. P. Budnikov, M. A. Matveev, and K. M. Tkachenko, Proc. Acad. Sci. USSR, 2, 121 (1951).

[7] P. P. Budnikov, and V. K. Gusev, Proc. Acad. Sci. USSR, 73, 5, 1009 (1951).

[8] N. P. Maximovsky, Accelerated method for the production of slag blocks. Coal Technology Press, Moscow (1950).

[9] I. T. Kudryashov, Autoclave cellular concrete and its use in building. State Building Press, Moscow (1949).

[10] P. A. Duvanov, Accelerated baking of bricks, Pub. by All-Union Central Council of Trade Unions, Prof. Press, Moscow (1950).

[11] P. P. Budnikov, Ceramic Technology, Kharkov, 224 (1927); 230 (1933); P. P. Budnikov, Building Industry, Nos. 11/12, 230 (1928); P. P. Budnikov, Achievements of Soviet science in the field of silicates during 30 years. Pub. by Institute of Local Constructional Materials, RFSFR, Moscow (1949).

[12] I. A. Kablukov, Crimean Salt Lakes, Moscow (1916); N. S. Kurnakov and others, Salt Lakes of the Crimea, Pub. by USSR Acad Sci., (1936); A. A. Alentev, Trans. 2nd Session on Refractory Materials, Inst. Metallurgy of the USSR Acad. Sci., Moscow, 208 (1941); P. P. Budnikov, Collected Scientific Researches on Building Materials, Technical Press, Moscow, 172-179, (1947).

Received May 2, 1951.

BEHAVIOR AND PROPERTIES OF THE OXIDES OF THE ALKALINE EARTH METALS IN SILICATE GLASSES[1)]

A. A Appen

In communications I and II [1, 2] methods were described for the determination of the partial properties of components (oxides) in complex glasses, and average numerical values for these partial properties $\bar{g}_i$ were found for a number of properties of alumina and the oxides of the alkali metals in silicate glasses.

Below are presented the results of an investigation of the partial properties $\bar{g}_{MeO}$ of the alkaline earth metals in silicate glasses, mainly 3-component ones of the type Me_2O-MeO-SiO_2. The mean partial properties of alumina and the alkali oxides have been taken as known and the values of $\bar{g}_{MeO}$ have been calculated by difference. In those cases where glasses of other types were involved, the calculation of the partial properties $\bar{g}_{MeO}$ was made when the average value of the partial quantities for the other oxides $\bar{g}_i$ entering into the composition of these glasses had been established.

EXPERIMENTAL

I. BeO. In Fig. 1 is shown the dependence on the composition of the system of the partial properties of beryllium oxide: the refractive index $\bar{N}_{BeO}$, the molecular volume $\bar{V}_{BeO}$, the mean dispersion $\bar{D}_{BeO}$, and the mean coefficient of linear expansion $\bar{\alpha}_{BeO}$ (20-400°C). On the average these dependencies can be expressed as straight lines parallel to the abscissa for all the properties examined. This linearity is maintained over the whole region of composition investigated, i.e. up to a content of 30% BeO in the glasses The dispersion of the points observed is practically always within the limits of experimental error. The results of investigations of the system Na_2O-BeO-SiO_2 will serve as an illustration. For example, the points corresponding to values of $\bar{N}_{BeO}$, calculated from Becker's data, fall systematically above those points found from the data of Lear and Silverman. For the partial molecular volume $\bar{V}_{BeO}$, the points are placed in the inverse order. Considerable divergencies were found between the properties of glasses of one and the same composition. In order to check these we synthesized and investigated 4 glasses from such systems and in the same region of composition. The results of our measurements fell between the data of the investigators mentioned above.

II. MgO. The material for the investigation of the properties of magnesia-containing silicate glasses is very scanty. The published numerical data on the optical properties of these glasses is practically non-existent. In order to fill this gap partially, we prepared some magnesia glasses and measured their optical constants, densities and coefficients of expansion.

As can be seen from Fig. 2, the partial refractive indexes, $\bar{N}_{MgO}$ in Na_2O-MgO-SiO_2 glasses, showed a strong tendency to increase, and the partial molecular volumesof MgO to diminish, as the magnesium oxide content in the glasses (shown by dotted lines) increased. This tendency is evidently due to the fact that sodium and likewise potash-magnesia glasses, in general, have an unusually low refractive indes and density (lower than in the corresponding beryllium glasses).

---

1) Communication III on the relation between the properties and composition of glasses.

Such low values for refractive index and densities of such types of glass must be considered anomalous. Later it will be shown that with other different combinations of compositions, magnesia glasses have higher values of the N_D and d than beryllium glasses of the same molecular composition. At large MgO contents (above 25-30%) magnesia glasses of the type Me_2O-MgO-SiO_2 also take an intermediate position between beryllium and calcium glasses relative to these quantities. Because of this it was considered impossible to average the partial values for the refractive index and molar volume of MgO; it was necessary to reckon with considerable changes in the latter. The correlation between the change in properties of glasses containing MgO should be subjected to more careful study. All the same, it can be taken that in complicated technical glasses the values of the partial refractive index and molar volume of MgO are close to values corresponding to the position of the solid line in the figure. In other, less accurately determined properties, the above-mentioned peculiarities in the behavior of MgO come out less clearly. The values for the partial mean dispersion and linear expansion coefficient of MgO may be taken as constant, as the MgO content in the glass rises from 0 to 25%.

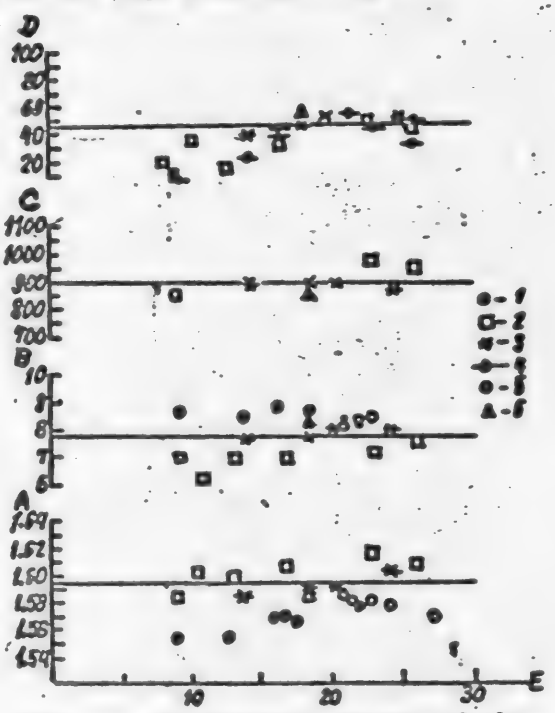


Fig. 1. Approximate values of the partial properties of beryllium oxide in silicate glasses.

A - $\bar{N}_{BeO}$; B - $\bar{V}_{BeO}$; C - $\bar{D}_{BeO} \cdot 10^5$; D - $\bar{\alpha}_{BeO} \cdot 10^7$; E - content BeO (in %). Origin of data for Na_2O-BeO-SiO_2: 1 - Lear and Silverman [3], 2 - Becker [3], 3 - Appen, 4 - Renker [3]; for K_2O-BeO-SiO_2: 5 - Lear and Silverman [3], 6 - Appen.

III. CaO. The properties of lime-silicate glasses are not identical and have been studied in detail by a number of investigators. Hence, our task in relation to these glasses was to make corresponding calculations and compare the results. All the same, we made some control glasses. Examination of the results of calculation (Fig. 3) shows quite clearly that the partial properties of CaO in the silicate glasses met with in practice, containing up to 25% CaO, may be taken as stable.

IV. SrO. The optical properties of strontia silicate glasses have not been investigated systematically up to the present time, because there is no practical interest in them. However, to obtain a complete picture of the behavior of the alkaline earth oxides in glasses, it was necessary to go into the properties of strontia glasses.

We prepared some glasses from the system Me_2O-SrO-SiO_2, and measured their optical constants, densities and coefficients of expansion. Our results to some degree fill the gap in our knowledge, and make it possible to put forward suggestions about the behavior and properties of SrO in glasses. As can be seen from Fig. 4, the behavior of SrO in glasses is characterized by a constancy of the partial properties and the properties of SrO may be expressed by definite numerical characteristics.

V. BaO. Definite conclusions about the behavior of BaO in silicate glasses can be drawn from Fig. 5. Barium oxide belongs to the group of oxides of elements of the second main group of the periodic table, which most definitely and over a

very wide interval of composition, are constant in their partial properties: The BaO in the glasses we prepared from the system $BaO - Al_2O_3 - SiO_2$ was brought up to 45 mole %, but in spite of this the properties of BaO remained practically unchanged.

Making the calculation of the partial quantities $\bar{\varepsilon}_{MeO}$ by difference, when the partial properties of the other components entering into the glass under examination are taken as known, does not, strictly speaking, give us thermodynamic partial values, but approximate and average ones. It is extremely important to establish the degree of approximation of these values to the thermodynamic ones. We made such an assessment experimentally for BaO. The corresponding results are set out in Table 1. The composition of the glasses investigated was such that the ratio SiO_2/Na_2O was constant at 3.75. The partial values $\bar{\varepsilon}_{MeO}$ were calculated from the thermodynamic Equation (5a) [1].

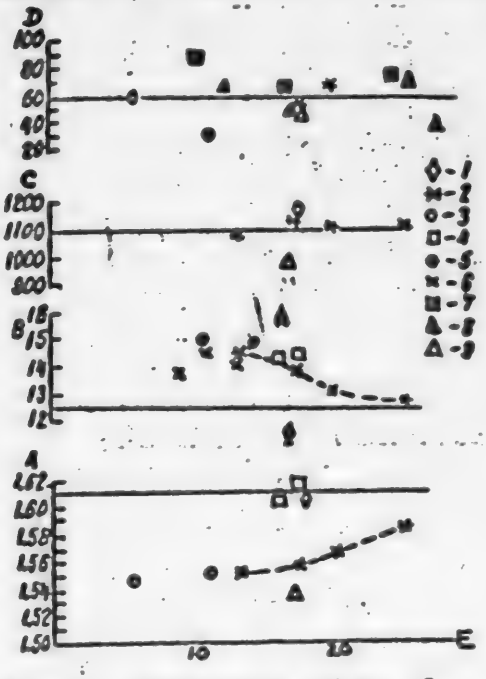


Fig. 2. Approximate values of the partial properties of magnesium oxide in silicate glasses

A-$\bar{N}_{MgO}$; B $\bar{V}_{MgO}$; C-$D_{MgO}\cdot 10^5$; D-$\bar{\alpha}_{MgO}\cdot 10^7$; E-MgO content (in %).

Origin of data for Li_2O-MgO-SiO_2: 1-Appen for Na_2O-MgO-SiO_2: 2-Appen, 3-Becker [3], 4-Lear and Silverman [3], 5-Peddle [3], 6-Inglis and Turner [3]; for Na_2O-MgO-PbO-SiO_2: 7-Parmelee and Shaw [4]; for M_2O-MgO-Al_2O_3-SiO_2: 8-Hall [5]; for K_2O-MgO-SiO_2: 9-Appen.

The average values of $\bar{N}_{BaO}$, $\bar{V}_{BaO}$, $\bar{D}_{BaO}$ and $\bar{\alpha}_{BaO}$, found directly, and by independent means, almost exactly agree with the average "difference" values of the corresponding magnitudes, indicated in Fig. 5 and Table 2. Such a result is a satisfactory indication of the correctness of our introduction of average numerical values for the partial properties of barium oxide. There is no doubt that such a test should be applied to our values found for $\bar{\varepsilon}_{MeO}$ and for other alkaline earth oxides.

Discussions of the Results

As is known, Winkelmann and Schott [10] in 1894 announced the additivity rule, according to which many properties of glasses can be calculated additively from the properties of the oxides contained in them. It was assumed that the additivity could be expressed in terms of the composition of the glass in weight % of the oxides. According to the additivity rule, the properties of a given oxide in a glass are determined only by its particular nature and do not depend on its quantity in the glass, nor on the nature of the other oxides present. For the characteristic properties of each of the oxides, it was proposed to determine numerical coefficients related to unit weight % of the oxides. Winkelmann and Schott's coefficients have been frequently corrected and extended. For example, to characterize the thermal expansion of oxides in glasses we know at the present time of no less than 16 series of coefficients proposed by different investigators.

By introducing such coefficients the authors either equated the properties of silica in complex glasses to the properties of pure quartz glass, and by

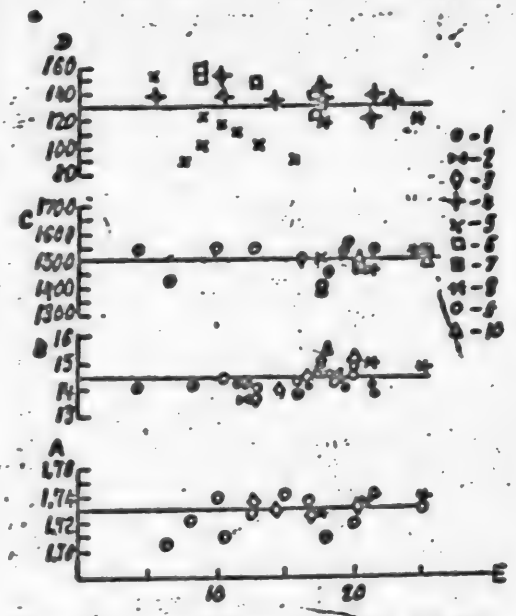


Fig. 3. Approximate values of the partial properties of calcium oxide in silicate glasses.

A - $\bar{N}_{CaO}$; B - $\bar{V}_{CaO}$; C - $\bar{D}_{CaO} \cdot 10^5$; D - $\bar{\alpha}_{CaO} \cdot 10^7$; E - CaO content (in %).

Source of data for Na_2O-CaO-SiO_2: 1-Morey and Mervin [3], 2-Inglis and Turner [3], 3-Safford and Silverman [6], 4-Schmid, Finn and Young [3], 5-Seddon, Turner and Winks [3], 6-Silverman [3], 7-Peddle [8] 8-Appen; for K_2O-CaO-SiO_2: 9-Morey and Mervin [8], 10-Peddle [3].

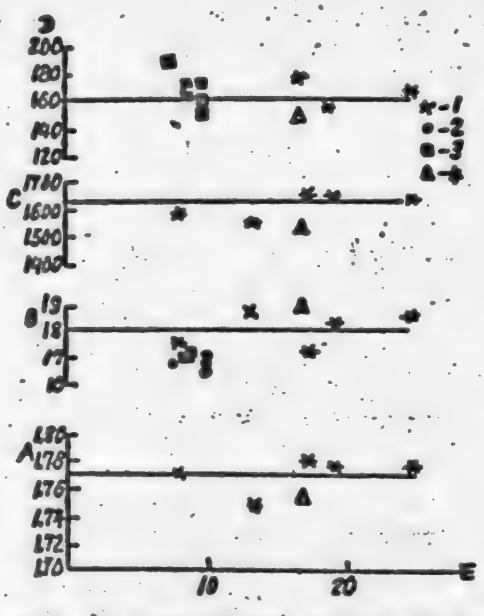


Fig. 4. Approximate values of the partial properties of strontium oxide in silicate glasses.

A - $\bar{N}_{SrO}$; B - $\bar{V}_{SrO}$; C - $\bar{D}_{SrO} \cdot 10^5$; D - $\bar{\alpha}_{SrO} \cdot 10^7$; E - SrO content (in %).

Source of data for Na_2O-SrO-SiO_2: 1-Appen, 2-Owens Illinois Glass Co. [8]; for Na_2O-SrO-Al_2O_3-SiO_2; 3-Owens Illinois Glass Co. [8]; for K_2O-SrO-SiO_2: 4-Appen.

TABLE 1

Partial Properties of BaO in Glasses of the Type Na_2O-BaO-SiO_2

Composition of glasses (in mole fractions)			Properties of glasses				Partial properties of barium oxide ($\bar{B}_{BaO}$)			
SiO_2	Na_2O	BaO	n_D	d	$(n_f - n_c) \cdot 10^5$	$\alpha_{30-400} \cdot 10^7$	N_{BaO}	V_{BaO}	$D_{BaO} \cdot 10^5$	$d_{BaO} \cdot 10^7$
0.7426	0.1980	0.0594	1.5176	2.652	898	116.4	1.898	20.85	1700	229
0.7010	0.1870	0.1120	1.5389	2.875	943	122.7	1.920	20.58	2107	219
0.6520	0.1740	0.1740	1.5654	3.144	1024	129.4	1.856	23.70	1895	180
0.6146	0.1640	0.2214	1.5821	3.330	1074	132.3				
			Mean				1.890	21.7	1900	210

difference calculated the coefficients for other oxides, or simply selected the most satisfactory combination of coefficients. Such methods do not seem to be scientific, because they introduce arbitrariness and multiple values into the

solution of problems, in particular when the properties of different types of glass are examined separately. By later and more accurate work, it was clearly shown that in general the additivity rule is not valid. Gelhoff and Thomas, Hilliard and Debrull [11] proposed to express the properties of the oxides by variable coefficients dependent, in a complex form, on the composition of the given oxides in the glass.

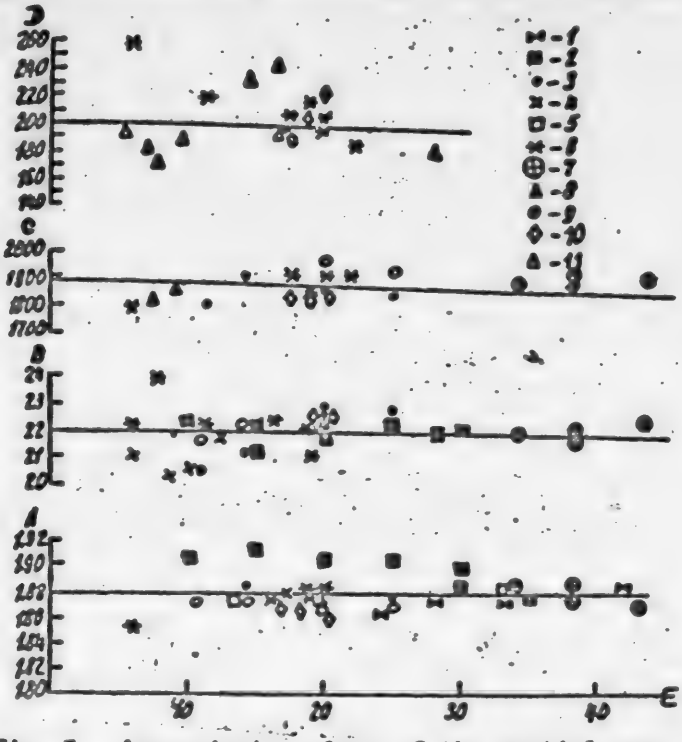


Fig. 5. Approximate values of the partial properties of barium oxide in silicate glasses.

A - $\bar{H}_{BaO}$; B - $\bar{V}_{BaO}$; C - $\bar{D}_{BaO} \cdot 10^5$; D - $\bar{\alpha}_{BaO} \cdot 10^7$; E - BaO content (in %).

Source of data for $BaO-SiO_2$: 1 - Escoll [3]; for $Na_2O-BaO-SiO_2$: 2 - Kumanin, 3 - Peddle [3], 4 - Inglis and Turner [3], 5 - Grin and Morgan [3], 6 - Appen; for $BaO-Al_2O_3-SiO_2$; 7 - Appen; for $Me_2O-MeO-BaO-Al_2O_3-SiO_2$; Hall [5]; for $K_2O-BaO-SiO_2$: 9 - Peddle [3], 10 - Appen, 11 - data for technical glasses.

Sun [12], proposed the utilization of such variable coefficients (for n_D) but took them as functions of the ratio of numbers of atoms of silicon to the number of atoms of oxygen in the glass (f_{Sc}) and not as functions of the quantity of component.

Very discouraging conclusions were formulated by Zhukovsky [13]. In 1934 he wrote: "The properties of separate oxides change differently in different types of glass...", and "it is impossible to get any general correlation from the study of any properties of glass".

The results of our work introduce considerable clarity into the question under examination. Zhukovsky's view, apparently, is correct only in the strictly theoretical sense and mainly relative to such properties of glasses as chemical stability, viscosity, etc., which change according to a very complicated law. The properties which we have examined change as a function of the composition of the glass much more simply, according to the rule expressed, and the behavior of many oxides relative to these properties can be described by simple formula if the composition of the glass is expressed not in weight, but in mole percentages of the oxides.

The material presented above shows that the partial properties of the oxides of the alkaline earth metals, as of the alkali metal oxides, are comparatively constant over a wide interval of composition, covering that usually met with in glass practice. Strictly speaking, the numerical characteristic $\bar{g}_i$ properties of these oxides in glass fluctuate in going from glass of one composition to another around some average value. However, the amplitude of the fluctuation is small in the majority of cases. It remains small not only when the composition is changed within the limits of a definite interval for one of the systems

given, but in going from one system to another. The comparatively large change in the partial properties of MgO in the ternary systems Me_2O-MgO-SiO_2, observed when completely replacing one alkali oxide by another, should preferably be referred to the phenomena which are rarer than usual. Thanks to this, it becomes possible to work out a simple and sufficiently accurate method for calculating the properties of technical glasses from their composition, and this we have done.[1)]

The average numerical characteristic partial properties of the oxides of alkaline earth metals in silicate glasses, as found by us, are set out in Table 2.

TABLE 2

Average Numerical Characteristic Partial Properties of the Oxides MeO in Silicate Glasses

Oxides	Average value $\bar{E}_{MeO}$				Limits of applicability of the numerical characteristics for oxide content in the glass (in mole%)
	$\bar{N}_{MeO}$	$\bar{V}_{MeO}$ (in cm^3/mole)	$\bar{D}_{MeO} \cdot 10^5$	$\bar{\alpha}_{MeO} \cdot 10^7$	
BeO...	1.595	7.8	890	45	0-30
MgO...	1.610 (1.57)[2)]	12.5 (13.5)[2)]	1110	60	0-25
CaO...	1.730	14.4	1480	130	0-25
SrO...	1.770	18.0	1630	160	0-30
BaO...	1.880	22.0	1890	200	0-40

Thus we came to the conclusion that the partial properties of the oxides of alkaline earth metals in glass, with some exceptions, mainly relative to MgO, do not depend to any considerable extent either on the quantity of the given oxide in the glass (within definite limits) nor on the nature of the other oxides present. Thus, we would appear to have re-established the rule of additivity in a new form. However, this is not so, because the partial properties of SiO_2 are always assumed to be variable [1]. Hence, if the partial properties of the oxide of the alkaline earth metals and likewise of the alkali metals remain always strictly constant, the properties of the glass do change as a function of the composition and these changes are represented on graphs by curved lines and by bent surfaces (it is true the curvature is small).

The additivity of certain properties, such as dispersion, can be spoken of only in the practical sense and that over a restricted composition range, qualitatively and quantitatively. Strict additivity of the properties of glass is in general not realized.

From Table 2 it is evident that the partial properties of oxides in going from BeO to BaO do not always change identically. If the value of $\bar{V}_{MeO}$, $\bar{D}_{MeO}$ and $\bar{\alpha}_{MeO}$ increase consistently, then there may be a minimum in $\bar{N}_{MeO}$ for MgO.

1) The proposed numerical characteristic properties of oxides in glasses, published earlier [14] has been subjected in our work to some corrections based on our own experimental material.

2) The values of $\bar{N}_{MgO}$ and $\bar{V}_{MgO}$ put in brackets are anomalous; they reflect the properties of the three component magnesia glasses of the type Me_2O-MgO-SiO_2.

It seemed of interest to give a comparison of the average partial properties of oxides in glasses with the properties of these oxides in the free state. Such a comparison of the properties of oxides is most complete and can be made most satisfactorily for the refractive index (Table 3).

Table 3

Comparison of the Average Partial Values $\bar{N}_{MeO}$ with the Average Refractive Index of Free Crystalline Oxides

Oxides	Average refractive index of the free crystalline oxides n_D [1])	Average partial refractive index of the oxides in the glass $\bar{N}_{MeO}$	$(\bar{N}_{MeO}-n_D)\cdot 10^2$
BeO	1.719	1.595	-12.4
MgO	1.736	1.610(1.57)	-16.6 to 12.6
CaO	1.837	1.730	-10.7
SrO	1.870	1.770	-10.0
BaO	1.980	1.880	-10.0

The refractive index (n_D) of the free crystalline oxides is considerably higher than the corresponding partial values of $\bar{N}_{MeO}$, the difference apparently showing a tendency to diminish as the molecular weight of the oxides increases. However, in spite of this tendency the largest difference $\bar{N}_{MeO}-n_D$ is shown not by BeO but by MgO.

Judged by the change in the refractive index, the density of the oxides examined ought also to diminish when introduced into glass. This actually happened with MgO. The data for the density of the other oxides cannot be taken as sufficiently reliable from handbooks. The density of the oxides varies within wide limits, depending on the manner of obtaining them.

Thus, on the one hand the oxides of the alkaline earth metals change their properties to a considerable extent in going from the free crystalline state to silicate glass, but on the other hand once in the glass their properties remain comparatively steady.

If the content of oxides in the glass is raised above the approximate limits indicated in Table 1, then the values $\bar{N}_{MeO}$ cannot be expressed by constant figures. Outside these limits, the $\bar{N}_{MeO}$ values commence to rise sharply, because the partial values $\bar{N}_{MeO}$ of the oxides of the alkaline earth metals in glasses considerably diminish relative to the n_D of the pure oxides. Actually such a tendency is most strongly seen in MgO, since the difference $\bar{N}_{MeO}-n_D$ for MgO is the largest.

Thus, the behavior of the oxides of the alkaline earth metals in glass, within the limits of certain limiting compositions, is opposite to the behavior of the oxides of the alkaline metals. While for the former there is a tendency for the numerical values $\bar{N}_1$ to increase with increase in quantity of the corresponding oxides in the glass, and with decrease in the silica content in the glass; for the latter under the same conditions there is a tendency for these values to decrease. This is evident as a result of the fact that the difference $\bar{N}_1-n_D$ is negative for the alkaline earths, while for the alkali oxides it is positive. Contradictory tendencies are observed for the values of the partial molar volumes. An attempt to correlate this phenomenon with the theory of the structure of glass will be taken up later.

In the present work we do not examine the various "fine details" on the property-composition curves for glassy systems. Our task is to establish the existence of the most general correlations which have the most decisive effect on the properties of glass and are of fundamental importance for theory. In the pursuit of such an aim it seems quite expedient to neglect abstractions, i.e. to separate the more

[1]) From the handbook "Physico-chemical Systems in Silicate Technology" (1949) by D.S.Belyankin, N.A.Toropov and V.V.Lapin.

general phenomena from the large number of complicating or partial phenomena. To the latter belong, above all, the phenomena associated with the differentiation of component parts of glass, leading to the formation of definite compounds in the glass under suitable conditions.

SUMMARY

In the strict formulation of the observed correlations the partial properties of the MeO oxides, as in all other components, should be taken as variables and as dependent on the composition of the glass. With increase in the molar content of the MeO oxides or with decrease in the SiO_2 content in the glass, the numerical values $\bar{g}_{MeO}$ have a tendency to increase rapidly in one definite direction, contrary to what is observed for the oxides of alkali metals.

This tendency is so weakly developed that in limiting, but wide regions of composition, the partial properties of the oxides MeO may be taken as constant.

LITERATURE CITED

[1] A.A.Appen, J.Appl.Chem. 24 (9) (1951).[1])

[2] A.A.Appen, J.Appl.Chem. 24 (10) (1951).

[3] G.W.Morey. The Properties of Glass (1938).

[4] C.W.Parmelee and D.Shaw, J. Am. Chem. Soc., 13, 408 (1930).

[5] F.P.Hall, ibid., 13, 182 (1930).

[6] H.W.Safford and A.Silverman, ibid., 30 (7), 203 (1947).

[7] W.Silverman, J.Soc.Glass.Tech., 24, 47 (1940).

[8] J. Am. Chem. Soc., 31 (1)(1948).

[9] K. Greene and W. Morgan, J. Am. Chem. Soc., 24, 111 (1941).

[10] A. Winkelmann and O.Schott, Ann.Phys.Chem., 51, 730 (1894).

[11] M.A.Matveev and B.A.Kleimeno. Calculations on Technical Glass. Light Industry Press (1938).

[12] K.H.Sun, J. Am. Chem. Soc., 30 (9), 282 (1947).

[13] G.Yu.Zhukovsky, Collection. "Glass Technique" (1934).

[14] A.A.Appen, Proc.Acad.Sci.USSR, 69 (6), 841 (1949).

Received June 10, 1950.

[1]) See Consultants Bureau English translation, p. 1027.

CAKING OF CARBONATES

A. Ya. Zvorykin

The problem of caking of carbonates on heating, as that of the halides, is of great importance. While in the study of the halides the phenomenon of caking depends basically on the state of aggregation, rate of heating, time of heating and temperature, with the carbonates there is added to these factors the dissociation of the carbonates above a definite temperature and likewise the interaction of the products of dissociation, oxides or their compounds, with the still undissociated or partially dissociated original substance. Consequently, in the study of the caking of carbonates we have a complicated phenomenon to deal with. In simpler cases, this may be looked upon as a two-component system: the undecomposed carbonate and the dissociated product, that is to say, the oxide.

Leaving a review of this question to later communications, which will involve examination of other experimental data, we shall dwell here on experimental results obtained with carbonates.

EXPERIMENTAL

This work was carried out by the method and in the apparatus described in our previous papers [1,2].

We examined the carbonates of lithium and sodium from the first group of the periodic table, and of beryllium, magnesium, calcium, strontium, cadmium and barium from the second. These salts can be divided into 3 groups on the basis of their ability to dissociate in the range 100-1000° which we covered in our studies: 1) salts which dissociate completely; 2) salts whose dissociation is fairly complete; and 3) salts whose degree of dissociation is small. Apart from this, some salts in this temperature range underwent polymorphic transitions.

In the work with chlorides we showed that a change of the amount of caking is bound up with the energy of the crystal lattice. Thus, the smaller the energy of the crystal lattice, the easier is diffusion and therefore under strictly identical conditions it would be expected that a large amount of caking should occur (so long as there is no influence, at these or other temperatures, of other accessory factors).

It seemed of interest to follow this question to more complicated cases, i.e., to the caking of carbonates.

Since in the literature there is no data about the energy of the crystal lattice for carbonates, we calculated it from Kapustinsky's formula.

$$U = 287 \cdot 2\frac{\Sigma n z_1 z_2}{r_1+r_2}\left(1 - \frac{0.345}{r_1+r_2}\right),$$

where $r_1 + r_2$ is the sum of the ionic radii (Goldschmidt); Σ_n is the number of ions in the molecule; z_1 and z_2 are the valencies of the ions.

The results of these calculations are given in the table on the next page.

From this table it can be seen that the crystal lattice energy of compounds in one group of the periodic system decreases from above to below, but metals of the sub-group such as zinc and cadmium differ somewhat; however, this relates to

Crystal Lattice Energies

Compounds	Radius of the cations according to Goldschmidt[3], r_1	Radius of the CO_3 ion according to Kapustinsky and Yatsimirsky [4], r_2	Crystal lattice energy, V
Li_2CO_3	0.78	1.85	569.4
Na_2CO_3	0.98	1.85	535.0
K_2CO_3	1.33	1.85	483.75
$BeCO_3$	0.34	1.85	852.2
$MgCO_3$	0.78	1.85	759.08
$CaCO_3$	1.06	1.85	696.0
$SrCO_3$	1.27	1.85	654.8
$CdCO_3$	1.03	1.85	702.01
$BaCO_3$	1.43	1.85	626.8

other properties of these metals. It must be remembered that the crystal lattice energy for the halides is considerably lower in absolute value. The amount of caking, as will be seen from the data given below, in those cases where sufficient values have been measured, increases with decreasing crystal lattice energy as is the case for the halides. But since here relationships are more complicated, there are some deviations.

In order to throw more light on the transitions which occur in the salts studied on heating, and likewise to get characteristics of the initial substances for certain salts, at our request Prof. Rode determined the heating curves and partially the cooling curves (in order to elucidate the possibility of conducting the process in reverse.[1])

Running briefly over the results obtained for each of the salts investigated for caking, we will dwell on some peculiarities of the two heating curves.

Among the carbonates of the first group we investigated those of lithium and sodium.

The caking of lithium carbonate was studied at 600, 650 and 800°. At 800° the salt had already begun to melt and had sharply changed in volume (by 50%). Caking at lower temperatures was insignificant and the sample always ran out when the apparatus was inverted. The loss in weight at 600 and 650° was 0.74-0.78% and at 800° it was 14.84%, while for complete dissociation it should be 65.71%.

Sodium carbonate, as data in the literature show, dissociates considerably at temperatures above 900°. At the temperatures of our experiments, the loss in weight was small: 0.7-0.92%. The amount of caking is shown by the curves in Fig. 1, which show a rapid rise at 750°. At 800° there was already a certain amount of fusion. Of the carbonates of the second group, we studied the following:

$BeCO_3$, $MgCO_3$, $CaCO_3$, $SrCO_3$, $CdCO_3$, and $BaCO_3$.

In the literature six basic beryllium carbonates are referred to, and one compound with four molecules of water. Our preparation, heated for 30 minutes at 700 and 900°, lost 52.46% in weight. This sample even at 900° did not cake very much (1 g of sample) [6].

From the published references to magnesium carbonate it is evident that the dissociation pressure of this salt at 540° is 747 mm Hg, and actually at 500° we found, from the change of weight, that all the carbon dioxide had been eliminated: the loss in weight, according to theory, should be 52.18%. The caking of this substance at all the temperatures selected (400, 500, 550, 700, 900, 1000° C) was very small; we did not manage to get any definite figures because the samples ran out when the apparatus was inverted.

[1]) Thermal diagrams for the carbonates of calcium and magnesium are given in the literature, hence they are not given by us [5].

The curves of strength of caking for calcium carbonate were obtained by us earlier, but in view of the sharp change in the degree of caking when dissociation becomes considerable, we repeated the results for calcium carbonate, obtained by precipitation. It should be noted that the dissociation pressure of calcium carbonate at 540° is very small (0.3 mm Hg), and a pressure of 760 mm is reached at 897°. The loss in weight on heating to 600° was insignificant, at 700° it was 3.76%, and at 800 it was 16.67%. The degree of caking at 200, 300, 500 and 600° was very small and equal, within the limits of our method, to a few grams; only at 700° and above did it rise sharply and approach some tens of kilograms. The general course of the curve, in spite of the fact that the work was carried out with a preparation whose composition was somewhat different, is similar to the curves obtained in the previous work. The high caking strength was conditioned by the presence of two phases, calcium oxide and calcium carbonate. The fact of considerable caking strength is extremely important. It would appear, at a first glance, that the extraction of CO_2 from the lattice, while it would not produce an important change, should leave some empty spaces in the lattice which should not cause a sharp increase in the caking strength, the more so because our experiments on caking of calcium oxide alone at 800° showed a small caking strength, 100 g on 0.95 cm_2, and 412 g at 1,000°. As also appears in the literature, calcium carbonate crystallizes in the rhombic system and calcium oxide in the cubic. Consequently, dissociation will cause a rearrangement of the lattice. This question was studied by X-ray, and requires separate independent investigation.

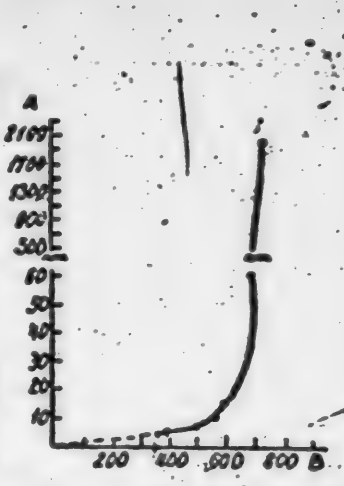


Fig. 1. Caking of sodium carbonate. A - strength of caking (g/0.95 cm_2); B - temperature (in °).

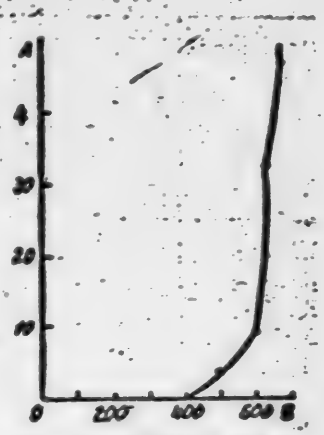


Fig. 2. Caking of strontium carbonate. A-strength of caking (g/095 cm_2) B-temperature (in °).

Corresponding to the fact that strontium carbonate dissociates at high temperatures, the loss in weight, within the limits of temperatures we studied, was some fraction of one per cent (0.75 - 0.99%). The caking strength at 400° was very small, 55 g, but at 500° it increased sharply and at 600, 650 and 700° it measured some tens of kilograms and at 800° it was 50 kg/0.95 cm^2 (Fig. 2).

The heating curve for cadmium carbonate showed a sharp endothermic effect, beginning at 305°; the minimum point was at 427°. This effect is very significant and is strongly marked not only on the differential curve but also on the heating curve. Apart from this, a number of other less important effects were observed on the curve (Fig. 3).

Consequently, the endothermic effect observed on the heating curves corresponds to the region of complete dissociation of the salt. Hence we carried out a considerable number of experiments in the region of this endothermic minimum, i.e., close to 427°. Apart from 4 determinations at 427°, determinations were made at 350, 390 and 434°. All these data permitted us to elucidate further to what extent the minimum of the heating curve is reflected on the caking strength curve, and we found that, at the temperature minimum, there is some lowering of the caking strength. Apart from the temperatures indicated, the strength of caking was also studied at 300, 450, 500, 600, 700, 800° C. The general appearance of the curves of caking strength is shown in Fig. 4.

Barium carbonate crystallizes in the rhombic bipyramidal system. It has two transitions: at 811° it goes over to the hexagonal system and at 983° to the rectangular system. At 811° the heat of conversion is -3.75 kcal/mole.

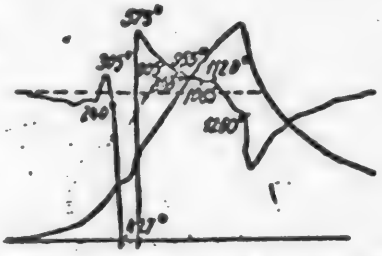


Fig. 3. Heating curves for cadmium carbonate

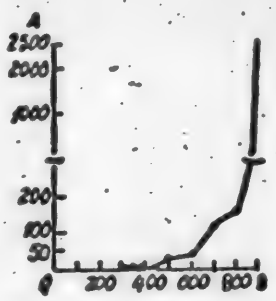


Fig. 4. Caking strength for cadmium carbonate. A - strength (g/0.95 cm^2); B - temperature (°C)

On the heating curves, Fig. 5, the endothermic effect is particularly important; it begins at 755° and ends at 915°. The minimum of this effect is at 785°. This effect is quite important; it is easily noted not only on the differential curve but also on the simple heating curve. A second endothermic effect lies between the temperatures of 915 and 1000°. Both these effects, as shown by the cooling curves, are reversible in character (955 and 755°). It should be noted that the effect at 755 is so considerable that it is quite discernible on the simple heating curve, on which there is a third minimum at 1240°. In the literature two transition points for barium carbonate, at 811 and 982°, are reported [7].

The data set out indicate that barium carbonate decomposes at still higher temperatures than those at which it was examined here. Within the limits of the temperatures used by us, this salt decomposes only by some fraction of one per cent (0.44 - 0.66%).

The caking strength varies from 160 g at 700° to 7110 g at 950°. A plot of this change is shown in Fig. 6.

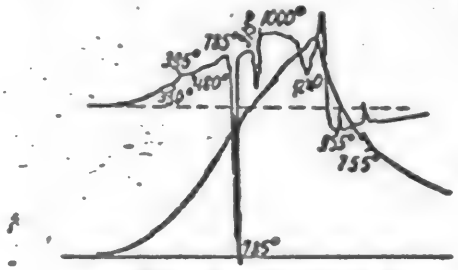


Fig. 5. Heating curve for barium carbonate.

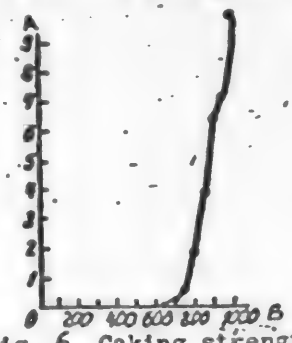


Fig. 6. Caking strength of barium carbonate. A - strength (kg/0.95 cm^2); B - temperature (°C).

SUMMARY

1. In the caking of carbonates, in spite of the complicated character of the process caused by dissociation, and the possibility of the formation of intermediate products and polymorphic transitions, the general course of the change of caking strength correlates with the crystal lattice energy, as was found also for the halides.

2. The caking strength for the salts studied changes regularly, depending on the place of the corresponding metal in the periodic table.

LITERATURE CITED

[1] A. Ya. Zvorykin and N.I.Timokhina, J.Appl.Chem., 22, 10, 1063 (1949).

[2] A. Ya. Zvorykin, Bull.Sec. Phys. Chem. Anal. XIX, 372 (1950).

[3] V. M. Goldschmidt, Ber., 1263 (1927).

[4] A.F.Kapustinsky and K.B.Yatsimirsky, J.Gen.Chem., 19, 12, 2191 (1949).[1)]

[5] L.G.Berg, A.V.Nikolaev and E.Ya.Rode, Thermo-Chemistry. Acad.Sci.USSR (1944).

[6] H.Copaux and C.Matignon, Bull., 37, 1359 (1925).

[7] A.I.Tsvetkov, Trans.Inst.Geolog.Sci., Acad.Sci.USSR, 120, 121 (1949).

Received December 20, 1950.

1) See Consultants Bureau English translation, p. a-665

BLANK
PAGE

THE GAS PHASE IN THE PROCESS OF ROASTING CHROMITE CHARGES

O.I. Pudovkina and N.A. Gushchina

Urals Institute for Chemical Research

It was shown earlier[1]) that the grains of chromite are oxidized by oxygen absorbed from the air by the liquid phase, with the formation in it of peroxidic compounds. The process of oxidation should depend on the intensity of absorption of oxygen by the liquid melt contained in the reaction mass and, consequently, on the composition of the gas phase. To introduce some clarity into these obscure questions it was interesting to study the effect of the oxygen concentration in the gas phase on the formation of sodium chromate.

EXPERIMENTAL

Starting materials. For compounding the charges the following materials were used.

1. Soda and oxides: chromium, magnesium, calcium and iron oxides were all chemically pure and completely anhydrous.

2. Ore from the Aktyubinsk deposits having the composition (in %): Cr_2O_3 46.63, Fe_2O_3 18.08, Al_2O_3 12.05, SiO_2 5.84, CaO 0.73, and MgO 13.00.

3. Dolomite of composition (in %): CaO 34.4, MgO 17.65, R_2O_3 1.08, and SiO_2 0.64. The ore and dolomite were ground so as to pass completely through sieve No. 70 and were dried to constant weight at 110°.

Method of investigation. The necessary quantities of components of the mixture were carefully stirred together and mixed in an agate mortar. The charge of weight, 3-4 g, was placed in a platinum boat in a layer 5-6 mm thick.

The apparatus for carrying out the experiment is shown diagrammatically in the figure. The boat with the charge was placed in a furnace previously heated to the necessary temperature, maintained at that temperature for a definite time, and then cooled in a desiccator. A pre-set mixture of nitrogen and oxygen, after passage through the furnace, was analyzed in an Orsat apparatus. Where necessary the nitrogen was freed from oxygen (2-8%) by passing it through a column filled with metallic copper, an ammoniacal solution of ammonium chloride, tubes containing a moisture absorbing compound, and a tubular furnace containing copper powder.

The finely ground product of heating was analyzed for chromium: hexavalent water soluble, acid soluble, and total. The % oxidation was calculated as the ratio of the sum of the water- and acid-soluble hexavalent chromium to the total.

The results of each experiment were obtained as the result of 2-3 experiments.

Effect of concentration of oxygen in the gas phase on the process of oxidation. In the first place it was of interest to conduct experiments with chemically pure materials, in order to diminish the number of factors simultaneously operating on the process of oxidation. The soda in the charge was always taken in stoichiometric quantities necessary for complete conversion of the Cr (III) to chromate. The weight ratios of the components, in experiments with pure chromium oxide were:

[1]) Cf. Ya. Vilnyansky and O.I.Pudovkina, J.Appl.Chem., 22, 683 (1949).

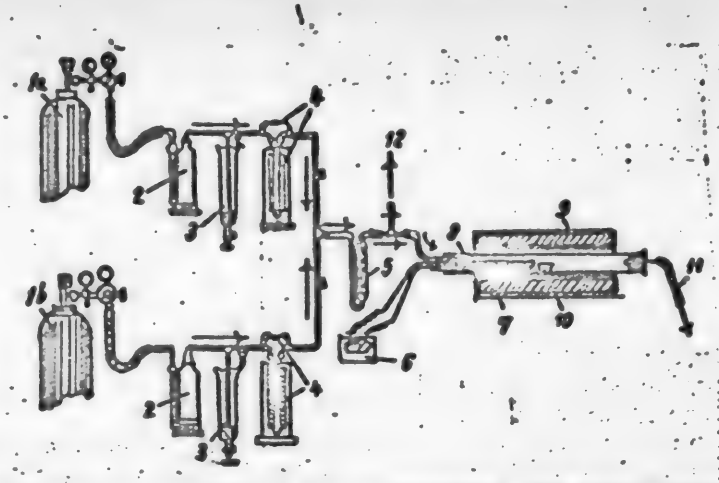


Fig. Layout of apparatus for conducting the experiments.
1a - Compressed oxygen bottle; 1b - Nitrogen bottle; 2 - Dreschel bottle with strong sulfuric acid; 3 - pressure-release device; 4 - Flow meter; 5 - Mixer; 6 - Millivoltmeter; 7 - Porcelain sleeve with Pt-PtRh-thermocouples; 8 - Glass tube for conveying the gases to the furnace; 9 - tubular furnace with platinum winding; 10 - platinum boat; 11 - lead-off tube; 12 - bleed for withdrawing gas for analysis.

Soda/chromium oxide/filler = 1.395:1:2.62.

The mixture was heated at 1150° for 30 minutes. Gas was passed through at 0.2 liters/minute. The results of the experiments are presented in Table 1.

Table 1

Effect of Oxygen in the Gas Phase on the Degree of Oxidation of Chromium Oxide. Temperature 1150°; duration of heating 30 minutes; gas rate 0.2 liters/minute.

Oxygen content in the gaseous mixture (in %)	Degree of oxidation of Cr_2O_3 at different fillings of charge (in %)			
	MgO	CaO	Cr_2O_3 [1]	Fe_2O_3
0.2	5.0	3.0	1.7	1.3
1.8	65.7	60.1	57.6	53.2
5.0	93.4	88.7	76.6	62.3
7.5	100.0	100.0	100.0	90.0
10.0	100.0	100.0	100.0	92.5

Table 2

Effect of Oxygen in the Gas Phase on the Degree of Oxidation of Chromite. Temperature 1150°; duration of heating 30 minutes; gas rate 0.2 liters/minute.

Oxygen content in the gaseous mixture (in %)	CrO_3 content in the heated mass (in %)			Degree of oxidation of chromite
	water soluble	acid soluble	total	
1.8	17.13	0.7	30.8	57.9
5.0	25.9	0.6	31.0	85.5
7.5	28.76	0.8	30.5	96.9
10.0	28.9	0.7	30.1	98.5
20.0	28.4	0.6	29.6	98.0

The data set forth show that with increase in the percentage oxygen in the gas phase the degree of oxidation of chromium oxide increases.

The products of roasting mixtures with iron oxide were compact cakes and, in experiments with 7.5-10% oxygen, there was a small amount of fusion, which also explains the lower percentage oxidation observed in these experiments. The liquid phase, formed here on the floor of the boat, in the absence of mixing, did not have sufficient contact with the oxygen for the latter to be absorbed very extensively, as a result of which the process of oxidation slowed down. In experiments

[1]) In these experiments, in calculating the percentage oxidation from the total hexavalent chromium determined by fusion with Na_2O_2, account was taken of the hexavalent chromium obtained from the Cr_2O_3 introduced into the charge as a filler.

with magnesium, calcium and chromium oxides, thanks to the good porosity of the heated mass, the absorption of oxygen by the liquid phase was more energetic.

In the products of heating of all the mixtures described, no acid-soluble hexavalent chromium was present.

The next series of experiments was carried out with charges composed of ore, soda and dolomite. The weight composition of the charges was as follows:

Soda/ore/dolomite = 0.65:1:1.07.

The results of these experiments are set forth in Tables 2 and 3.

Table 3

Effect of Oxygen in the Gas Phase on the Degree of Oxidation of Chromite. Temperature 1150°; duration of heating 5 minutes; gas rate 0.2 liters/minute.

Oxygen content in the gas mixture (in %).	CrO_3 content in the heated mass (in %)			Degree of oxidation of chromite (in %)
	water soluble	acid soluble	total	
10	24.83	0.72	29.2	87.5
20	26.5	0.59	29.8	91.2
30	27.47	0.39	29.8	93.4

By comparing the results of Tables 1 and 2 it is evident that the chemical behavior of chromite is the same as that of pure chromium oxide. The degree of oxidation of the ore increases with increase in the oxygen concentration in the gas.

In the following experiments, the effect of the gas rate, and of the total quantity of oxygen passed, on the oxidation was studied. The results obtained are set out in Table 4.

Table 4.

Effect of Gas Rate and Oxygen Content in the Gas Phase on the Oxidation of Chromite Temperature 1150°; duration of heating 30 minutes.

Oxygen content in the gas mixture (in %)	Quantity of oxygen passed relative to the theoretically required quantity									
	5.28		3.96		2.64		0.95		0.5	
	ml per minute	% oxidation	ml per minute	% oxidation	ml per minute	% oxidation	ml per minute	% oxidation	ml per minute	% oxidation
10.0	200	98.5	150	98.0	100	98.0	36	94.0	19	47.0
7.5	266	98.0	200	96.9	133	98.0	48	92.0	25	46.0
5.0	400	96.0	300	90.0	200	85.5	72	63.0	38	36.0
1.8	1100	90.0	831	88.5	554	77.3	200	57.9	105	24.0

From the data of Table 4 it follows that with a content of oxygen less than 7.5-10.0% in the gas phase, the degree of oxidation of chromite increases with increase in concentration of oxygen and gas rate. However, even with an excess of the total oxygen passed, of many times over the theoretical, the percentage oxidation of the chromite remains low.

When using gas with 7.5-10% oxygen a change in the rate of passage of gas scarcely affected the percentage oxidation of the ore, when the total quantity of oxygen passed was not less than the theoretically required quantity.

In the roasting of chromite with soda and dolomite, an oxygen content in the gas passed through the furnace not lower than 7.5-10% should be taken as an index for the presence of sufficient oxygen in the gas phase for oxidation. This is in agreement with industrial data.

SUMMARY

1. The oxidation of chromite charges depends on the oxygen concentration in the gas phase, on the gas rate, and on the total quantity of oxygen passed.

2. In order to obtain a high percentage oxidation of the chromite, the oxygen concentration in the furnace gas ought not to be lower than 7.5-10%.

Received November 20, 1950.

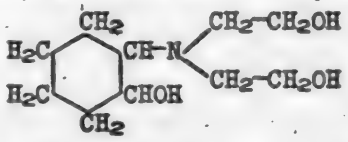
CONDENSATION OF CYCLOHEXENE OXIDE WITH DIETHANOLAMINE AND MORPHOLINE

A. A. Ponomarev and R. N. Sablina

Department of Organic Chemistry of the N. G. Chernyshevsky
Saratov State University

Like other α-oxides, cyclohexene oxide interacts with ammonia and different amines, forming the corresponding amino alcohols. On heating it with aqueous ammonia in a sealed tube, cyclohexene oxide yields cis-2-aminocyclohexanol [1]; when saturated alcoholic ammonia is used bis-(2-hydroxycyclohexyl)-amine is obtained, essentially in two forms. With ethylamine, cyclohexene oxide gives cis-2-ethylaminocyclohexanol-1, and bis-2-(hydroxycyclohexyl)-ethylamine; with diethylamine, cis-2-diethylaminocyclohexanol-1 is obtained.. Aniline and methylaniline form correspondingly: cis-2-anilinocyclohexanol-1 and cis-methylanilinocyclohexanol [2]. Products of condensation of cyclohexene oxide with piperidine and piperazine are known [3]. The reaction of cyclohexene oxide with ethanolamine was studied by Mousseron and Combes, [4], who obtained, on heating a mixture of both substances in alcoholic solution for 6 hours at 120°, 2-(2-hydroxyethylamine)-cyclohexanol-1, a crystalline product melting at 68° and boiling at 185° at 15 mm; the m.p. of the hydrochloride was 145°. The authors suggested that they had obtained the trans form. The ability of the substance to form a characteristic copper complex was noted.

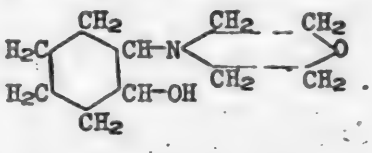
In their paper these authors mention the condensation of cyclohexene oxide with diethanolamine, forming 2-(bis-2-hydroxyethyl)-aminocyclohexanol-1.



which they describe as a liquid boiling at 195° at 1 mm; the hydrochloride had a melting point of 122°. This product also formed a copper complex.

We have carried out the condensation of the cyclohexene oxide with diethanolamine and morpholine with the object of obtaining the corresponding amino alcohols. This showed that from cyclohexene oxide and diethanolamine there is formed, in quantitative yield, 2-(bis-2-hydroxyethyl)-aminocyclohexanol which, however, is a crystalline substance melting at 47-48°, and not a liquid as is stated in the paper of Mousseron and Combes. It is possible that under the experimental conditions they employed, and under ours, different forms of this product are produced.

The condensation of cyclohexene oxide with morpholine proceeds easily on moderate heating of the equimolecular mixture of the reactants and leads to the formation, in good yield (78% of theory), of N-(2-hydroxycyclohexyl)-morpholine,



The latter was obtained as well formed, slightly yellowish crystals of m.p. 36-37°. The hydrochloride was a white crystalline product, melting at 218-219°.

The characteristic microscopic reaction with cadmium acetate, applied to this compound, produced characteristic tabular crystals, insoluble in water, ether, alcohol, benzene and carbon tetrachloride. Apparently, this reaction can serve for the identification of N-(2-hydroxycyclohexyl)-morpholine; its use for the detection of Cd^{++} is not excluded, since Cu^{++}, Bi^{++}, Zn^{++}, Pb^{++}, Hg^{+} and Hg^{++} do not form precipitates.

EXPERIMENTAL

Cyclohexene oxide was obtained from cyclohexanol via cyclohexene and chlorocyclohexanol [5]. After three redistillations it was obtained as a liquid boiling at 129-134°.

Commercial diethanolamine was used: it was redistilled in vacuum; crystals, m.p. 28°. Morpholine was used in the form of a liquid boiling at 128-130°.

2-(Bis-2-hydroxyethyl)-aminocyclohexanol-1. In a flask, fitted with a reflux air condenser, a mixture of 9.8 g of cyclohexene oxide and 10.5 g of diethanolamine was placed and heated on an oil bath at 125° for 2½ hours, and afterwards for a short time at 150°. In this way a homogeneous liquid was obtained (the initial components did not mix before heating together). The reaction mixture was allowed to stand in the cold, and on the second day crystallization of the mass commenced: in a short time the whole mass set solid A product with a m.p. of 47-48° was obtained. Attempts to recrystallize the product were not successful on account of the good solubility of the product in the majority of organic solvents: ether, benzene, chloroform, ethyl and methyl alcohols, and carbon tetrachloride.

To purify the substance it was distilled in vacuum. A fraction, weighing 19.6 g and boiling at 207-208° at 3 mm, was obtained; it was a colorless oil, which on standing crystallized once again. Under the microscope the crystals were seen to have a fine-grained structure, in places forming fibrous aggregates, anisotropic, active (to polarized light). n = 1.6, m.p. 47-48°.

Analysis

0.1076 g substance: 0.2325 g CO_2; 0.0964 g H_2O.
C.1122 g substance: 0.2414 g CO_2; 0.1088 g H_2O.
Found %: C 58.95; 58.72; H 10.02, 10.85.
Calculated %: C 59.13; H 10.42.
0.1498 g substance: 9.3 ml N_2 (22°, 766.5 mm).
Found %: N 7.29.
$C_{10}H_{21}O_3N$. Calculated %: N 6.89

The hydrochloride was obtained by passing a stream of dry HCl through a solution of the substance in absolute ether. White crystals which, when washed with ether and dried in a vacuum dessicator, had an m.p. of 155-158°.

With Dragendorf's reagent [6] (potassium-iodine-bismuth) 2-(bis-2-hydroxyethyl)-aminocyclohexanol formed a crystalline deposit which was claret in color; the impure crystals melted at 155-158°.

N-(2-hydroxycyclohexyl)-morpholine. A mixture of 9.8 g of cyclohexene oxide and 8.7 g of morpholine was heated in a flask, with a reflux air condenser, on an oil bath at 120-125° for 7 hours, and afterwards for 7 hours at 130-140° with the addition of some drops of concentrated acetic acid. On distillation in

vacuum a fraction was obtained with a b.p. of 145-147° at 15 mm, and weighing 14.5 g (78% of theory). The oil was straw-yellow, hygroscopic, and did not change on storage for several months, but on addition of crystals, which had been obtained by the condensation of cyclohexene oxide with diethanolamine, the liquid crystallized within a few minutes.

Under the microscope these were seen to be large, well formed, transparent, anisotropic crystals, n = 1.63, b.p. 36-37°

Analysis

0.1630 g substance: 0.3851 g CO_2; 0.1502 g H_2O.
0.1230 g substance: 0.2910 g CO_2; 0.1196 g H_2O.
Found %: C 64.47, 64.56; H 10.31, 10.88.
Calculated %: C 64.83; H 10.34.
0.2145 g substance: 15.5 ml N_2 (24°, 755 mm).
Found %: N 7.91.
$C_{10}H_{19}O_2N$. Calculated %: N 7.55.

Determination of the percentage hydroxyl group content by Werle's method [7]:

0.2160 g substance: difference between the titer of the blank and the solution under investigation 2.23 ml of 0.5 N KOH (K = 1.0352).

Found %: OH 9.00.
$C_{10}H_{19}O_2N$. Calculated %: OH 9.13.

The hydrochloride was obtained as described earlier: white crystals melting at 218-219° (after washing with absolute ether and drying in a vacuum dessicator).

With Dragendorf's reagent a bright red, crystalline precipitate was formed; the unpurified crystals melted at 173-180°.

N-(2-hydroxycyclohexyl)-morpholine dissolves well in cold ether, benzene, and alcohol. It is hygroscopic.

When a drop of 0.1% cadmium acetate and a drop of N-(2-hydroxycyclohexyl)-morpholine are mixed on a watch glass, characteristic, well-formed tabular crystals appear after about 40 minutes.

The crystals are insoluble in water, ether, alcohol, benzene, and carbon tetrachloride.

SUMMARY

It has been established that 2-(bis-2-hydroxyethylamine)-cyclohexanol is a crystalline substance melting at 47-48°.

LITERATURE CITED

[1] L. Brunel, Comptes rend., 137, 199 (1903).

[2] L. Brunel, Ann. Chim. Phys. (8) 6, 254-262 (1905).

[3] Kussner, Chem. Zentr., 2, 1358 (1933).

[4] M. Mousseron and Combes, Bull., 82-83 (1947).

[5] Synthesis of Organic Substances. Collection 1. State Foreign Literature Press 322, 496, 509 (1949).

[6] G. Clark, Handbook on Qualitative and Quantitative Analysis. (Russ. Ed.) United Sci. Tech. Press, 282 (1934).

[7] K. Andrianov and D. Kardashov, Practical work on synthetic resins. State Chem. Inst. 140, 1946.

Received August 26, 1950.

BLANK
PAGE

THE ROLE OF COMPLEX SILVER COMPOUNDS IN PHOTOGRAPHIC DEVELOPING

N. M. Zyuskin

It is taken for granted that in the process of photographic developing only the surface grains of silver bromide are reduced. This opinion is confirmed by microscopic observation of the development of single layer preparations of photographic emulsions. However, such preparations do not reproduce all the conditions of development of the usual photographic layer, because in the latter the grains of silver bromide are at a considerably smaller distance from one another [1], and also the conditions for the diffusion of the developer solution and of the products of oxidation are different from those in single layer emulsions.

It is known that in developer solutions containing considerable quantities of sodium sulfite or other silver bromide solvents, which form dissolved complex silver compounds, chemical development is accompanied by physical development, i.e. by the reduction of silver from the solution.

It has been noted [2] that, in the treatment of images on silver bromide emulsions, the contrast of the image is larger when solvents for silver bromide are introduced into the first developer than when the layer is treated with silver bromide solvents after the solution of the silver image in the second developer. This suggests that the grains of silver bromide, immediately adjacent to the developed grains, develop more rapidly than the rest of the grains.

Gorbachev, Bogomolov, and Shcherbachev [3], discovered that on prolonged development with energetic alkaline organic developers, the contrast of the image formed was considerably enhanced. The authors suggested that those grains of silver bromide, lying close to the developed grains, were dissolved by the potassium bromide formed in the process of development.

As microscopic observation of the process of development in the usual photographic layers appears impossible, since the grains of silver bromide cover over one another in projection, we used combined photographic layers, composed of two layers, which may be brought in contact or separated at any desired stage of the process. Layers in close contact can be examined as a single layer. Such methods are used in photographic technique (ozobrome, diffusional transformation, see Rott [4]).

EXPERIMENTAL

The combined photographic layers which we investigated were of two kinds: 1) layers in which diffusion into the developer solution was excluded; and 2) layers with free diffusion into the developer solution.

The first variant was prepared as follows: One layer was usually a positive cine film, while the second layer was prepared from special plates by pouring on a separate silver emulsion of such composition, that after complete reduction of all the silver bromide, the maximum optical density did not exceed 2.5.

The usual photographic image was obtained on the positive film (stepped wedge), by development in Chibisov's metol-hydroquinone, and was fixed in acid fixer with subsequent prolonged washing in tap water. Half the wedge was cut off and served as a control. After this, the washed and fixed image on the

positive cine film was treated with developer for a prolonged time (30 minutes). The unexposed plates were immersed in the same developer for 30 seconds. Then both layers were brought into contact with their emulsion sides facing, and were held together with clips. After a definite time of contact the layers were separated from one another, the film washed and dried, and the plates, after washing, were exposed and developed to complete reduction of all the silver bromide in the layer.

Developer Agfa-12 was used, containing, per liter: 12 g metol, 100 g sulfite, 5.75 g of Na_2CO_3 and 2.5 g of KBr.

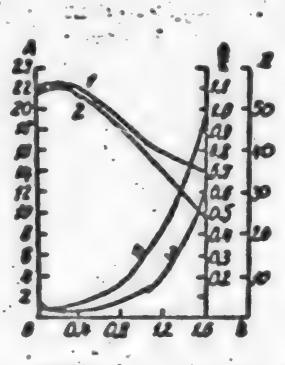


Fig.1. Effect of silver on the solution of silver bromide, Developer Agfa-12.
A-solubility of AgBr(mole/liter)
B-KBr content (in moles)
C-Density (D);D-ΔD (in %).
Refer to the text for the meaning of the figures on the curve.

As a result of 15 minutes contact with it, an image of the wedge was formed, and so the density of the image obtained was inversely proportional to the density of the wedge. Thus, the silver bromide in the emulsion layer, impregnated with developer, was exposed to strong solvent action at those parts which were in the immediate neighborhood of metallic silver. The image which had been brought into contact, developed, and fixed, was strengthened to a greater or lesser extent, corresponding to the fall in the density of the plate.

The water layer between the emulsion layers in contact was small. During the time of contact the layers were placed between plates under a pressure varying from 10-75 g/cm^2. The results obtained by this technique were practically identical.

The results of the investigation, using the Agfa-12 developer with different potassium bromide contents and keeping the layers in contact for 15-minutes, are shown in Fig.1, in which Curve 1 relates to the density of the plates after reducing the silver bromide, adjacent to those parts of the layers in contact, in which silver was absent; Curve 2 relates to the density of the same plates coming up against a definite density of the silver image; Curve 3 relates to the difference between these densities in percentages and indicates the more rapid solution of the silver bromide in the presence of silver; Curve 4 shows the solubility of silver bromide in the given developer, from data of Lyalikov and Razumova [5]. A clear correlation can be seen between the last two curves, indicating that this process depends on the solubility of the silver bromide in the given developer, conditioned among other things by the concentration of the potassium bromide.

Such an acceleration of the solution of silver bromide in the presence of silver present in the layer was not observed when using developers which did not contain silver bromide (iron developer).

We determined the solubility of silver bromide in solutions containing 40 g/liter $Na_2SO_3{\cdot}7H_2O$ and 25 g/liter Na_2CO_3 (excluding the developer substance) as a function of the concentration of potassium bromide, by the method described by Lyalikov and Piskunova [6], which involves titration with a solution containing 10 g/liter of silver nitrate until a turbidity appears; the solution must be stirred vigorously during the time of titration. By the same method, the solubility of silver bromide in this solution was determined in the presence of sodium thiosulfate (0.005 and 0.03 mole/liter); in each titration the complete solution of the deposit in excess of the titrating solution was confirmed. The data obtained are set forth in the Table.

Solubility of silver bromide in solutions containing 40 g/liter $Na_2SO_3 \cdot 7H_2O$, 25 g/liter Na_2CO_3 in the presence of variable quantities of potassium bromide and sodium thiosulfate at 20°

Quantity of KBr		Solubility of AgBr (g/liter)		
mole per liter	g per liter	without $Na_2S_2O_3$	with 0.005 mole/liter $Na_2S_2O_3$	with 0.03 mole/liter $Na_2S_2O_3$
0.01	1.19	0.0407	0.5557	2.880
0.02	2.38	0.0275	–	–
0.03	3.57	0.0231	–	–
0.04	4.76	0.0187	–	–
0.05	5.9	0.0165	0.3247	–
0.1	11.9	0.0132	0.2566	1.819
0.2	23.8	0.0132	0.1845	1.525
0.4	47.6	0.0253	0.1331	1.305
0.6	71.4	–	0.1417	–
0.8	95.2	0.0659	0.1760	1.187
1.6	190.4	0.3599	0.4794	1.336

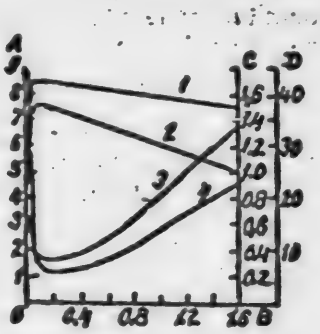


Fig. 2. Effect of silver on the solution of AgBr. Chibisov developer. A) AgBr solvent (moles·10^3); B) KBr content (moles); C) density (D); D) ΔD (%). Meaning of the figures on the curves will be found in the text.

The results of investigations of the Chibisov developer with 15-minutes contact at 20° are given in Fig. 2, in which the meaning of the figures is as in Fig. 1. The results of investigating the Chibisov developer containing sodium thiosulfate in combined layers are given in Fig. 3 (different concentrations of thiosulfate at one and the same time) and in Fig. 4 (different times for one and the same concentration of thiosulfate). From an examination of these curves it is seen that the quantity of silver bromide dissolving, under the influence of metallic silver, is proportional to the quantity of the latter, by measurement of optical density, but within definite limits, beyond which the curve becomes parallel to the abscissa axis.

Films were taken, instead of plates, for contact experiments. After reducing the silver bromide contained in them, transverse sections were prepared from them; a microphotograph of one of these is shown in Fig. 5 [1]). It can be seen that in the surface layer, at those places which came up against a silver image, silver is absent. The thickness of the layer in which silver is absent, designated δ, is proportional to the density of the silver image in immediate contact with the part of the film concerned. Thus, the radius of action of the silver particles depends on the solubility of AgBr in the given developer and on the time of treatment. From an examination of Figs. 1 and 2, it can be deduced that the process of solution of AgBr in the presence of Ag proceeds at a sufficient rate at high concentrations of potassium bromide.

The results obtained in investigating the development of layers in contact, one of which lay up against exposed silver bromide (graded wedge) and the other of which was uniformly exposed, using a developer containing 8 g/liter of sodium thiosulfate, are shown in Fig. 6. Depending on the intensity of exposure of the second layer and consequently on the quantity of soluble bromide formed, there was a deceleration of the dissolution of silver bromide at those places which were up against the developed image having the greatest exposure. This phenomenon may be explained by a depression of the solubility of silver bromide by the bromide solutions liberated on development of the heavily exposed parts. As emerges from the Table, the increase in concentration of potassium bromide above 0.4 mole/liter, in a developer solution containing 0.03 mole/liter sodium thiosulfate, did not produce a sharp increase in the solubility of silver bromide.

[1]) See Plate, p. 1387.

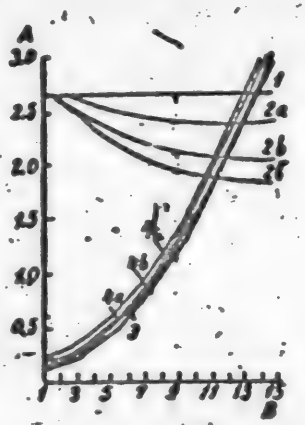


Fig. 3. Effect of silver on the dissolution of AgBr. Chibisov developer with sodium thiosulfate. Time of development 15 min.
A - density (D); B - log H (No. of field on sensitogram).
1. Plates at positions not in contact with silver; 2. Plates in contact with Ag: a - 1 g/liter, b - 4 g/liter, c - 8 g/liter; 3. Initial silver image; 4. Image after contact: a - 1 g/liter, b - 4g/liter, c - 8 g/liter.

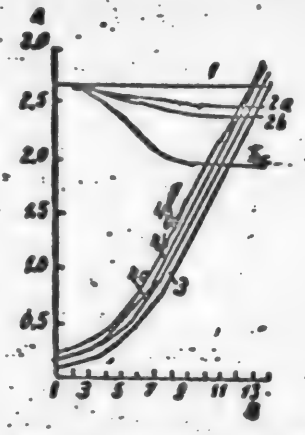


Fig. 4. Effect of silver on the dissolution of AgBr. Chibisov developer with 8 g/liter sodium thiosulfate.
A - density (D); B-log H (No. of field on sensitogram).
1. Plates at positions not in contact with silver; 2. Plates in contact with Ag: a - 3 minutes; b - 9 minutes; c - 12 minutes; 3. Initial silver image; 4. Image after contact: a - 3 minutes; b - 9 minutes; c - 12 minutes.

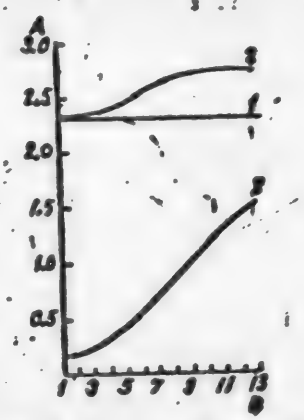


Fig. 6. Development of two exposed layers in contact.
A - density (D); B - log H (No. of field on sensitogram).
1 - Uniformly exposed plates in places not in contact with silver; 2 - Plates in contact with developed silver; 3 - Image in second layer.

From the graphs in Figs. 3 and 4, the extent to which physical development participates in the formation of the image by chemical development may be grasped. The increase in the density of the silver image in the given time of contact approximately corresponds to the quantity of silver produced as a result of physical development.

The same correlation was observed also in combined layers with free diffusion into solutions, which were prepared as follows: diapositive plates already having a silver image (developed, fixed and washed), or with exposed layers, were strongly hardened with formalin; after washing the layer was removed from the glass and placed on the exposed or unexposed diapositive plates and dried. Development in Chibisov developer is mainly chemical under these conditions; the process of solution of neighboring grains of silver bromide with later reduction of the silver from the solution is a slower process. It is evident that the relative rate of these two processes is determined by many factors and may be very different.

Although the combination of photographic layers does not entirely reproduce all the conditions of development in the normal photographic layer, it can be assumed that the correlations observed should be of still greater importance

in the latter in view of the smaller distance between the grains of silver bromide.

The explanation of the acceleration of the dissolution of silver bromide brought about by metallic silver should be sought for in the fact that, as a result of the reduction of silver by the catalytic action of metallic silver, there is a displacement of the equilibrium with liberation of solvent, which can then act on the silver bromide; in this the diffusion of developer from the layer into the developing solution is evidently a slower process.

This is illustrated by the results of development, introducing sodium thiosulfate into the developer solution at different stages of development.

Chibisov's developer, containing 8 g/liter sodium thiosulfate was used. The sensitogram was divided into two parts, both halves were placed in the developer without thiosulfate, and after a certain time some sodium thiosulfate was introduced into the developer for one of the halves. The total time of development was 6-minutes for both halves.

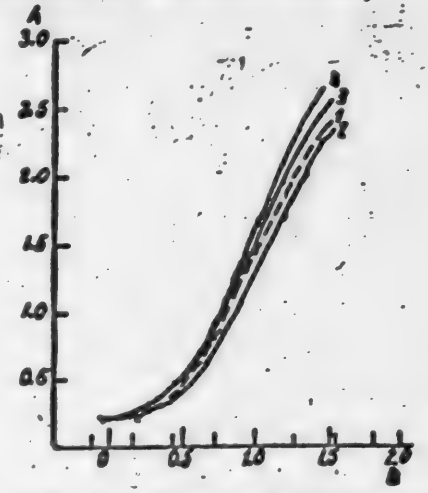


Fig. 7. Effect of addition of $Na_2S_2O_3$ on development. A - density (D); B - log H. 1 - Without $Na_2S_2O_3$, time of development 6 minutes; 2 - 8 g/l $Na_2S_2O_3$ added 1 min. after the commencement of development; 3 - Ditto, after 2 minutes; 4 - Ditto, after 4 minutes.

The results obtained are shown in Fig. 7. It can be seen that while the addition of sodium thiosulfate to the developer in the initial stages of development lowers the amount of silver appearing, the addition of this salt to the developer in the final stages increases the amount of silver that is reduced at the expense of the dissolved complex compounds.

Thus in many cases of photographic development, the photographic layers cannot be considered as an isolated system of exposed and developed silver bromide grains distributed among unexposed grains. Other grains of the layer take part in the formation of the image, mainly those near to the developing grain. In some cases, depending on the properties of the developer, the solution of these grains may be slow compared with that of the other grains. This interaction of the developing with the unexposed grains should be taken as a feature of those photographic processes, in which unexposed grains (transformation, diffusional transformation, Sabbat effect) are utilized for the formation of the image.

Methods of transforming the image in slow developers are known in which the positive image consists of a dichroic fog, absent from those places where there is a normal negative image. Such phenomena also occur to a larger or smaller degree in ordinary photographic development, in particular they are among the different factors which cause fogs. It is known that fog diminishes as the density of the image increases.

Stevens's and Norrish's [7] hypothesis, that the dispersion of metallic silver in the initial stages of development around the developing grains of silver bromide is the cause of desensitization in the Sabbat effect, seems doubtful in the light of the above.

The basic cause of the effect of adjacent regions is taken, at present, to be the lateral diffusion of developer and of the products of oxidation of the developer solution into the layer. Other explanations have been given in the past. They arise from the theory of supersaturation and, according to them, as a result of the formation of a saturated solution of silver, a further quantity of this element separates at the edges of the image.

We made microphotographs of the appearance of the edge of the fixed silver image, used in the combined photographic layers before and after contact with layers containing silver bromide; these are shown in Figs. 8 and 9.[1] A considerable increase in the density of the image can be seen; the explanation of this phenomenon should be related to the fact that the silver at the edge of the image is surrounded by a large quantity of silver bromide.

The reduction of silver from the dissolved complex compounds has a definite importance on a number of other factors which are reflected in the effect of adjacent sites. This can also explain the increase in density of the image when sodium thiosulfate is introduced into ordinary developer [8]. Such a phenomenon should occur to an even larger degree in those cases where developed metallic silver is present in developing the exposed layer. This may happen in the Sabbat effect

Fig. 10[1] is a microphotograph of the edge of the image obtained when sodium thiosulfate is introduced into the developer, used for the secondary development after diffusional inoculation; in Fig. 11[1] is shown the same image obtained without introducing sodium thiosulfate into the secondary developer. A considerable strengthening of the adjacent sites effect can be seen in the first case.

SUMMARY

1. In many cases of photographic development the unexposed grains of silver bromide which lie near to the exposed ones take part in the formation of the image, and they dissolve more rapidly than the remaining grains of silver bromide in the layer.

2. Depending on the formula for the developer, in certain cases there is also a delay in the solution of the unexposed grains which are close to the grains undergoing development.

3. The reduction of silver from dissolved complex compounds appears to be one of the causes of the adjacent site effect.

LITERATURE CITED

[1] G.P.Faerman, Nature 38, 3, 19 (1949).

[2] N.M.Zyuskin and E.K.Ostryanskaya, Cinechemicophotographic Industry, 8, 41 (1937).

[3] B.K.Gorbachev, K.S.Bogomolov and K.O.Shcherbachev, Cinechemicophotographic Industry, 8, 40 (1940).

[4] A. Rott. Science et Industries Photographiques, 13, 151 (1942).

[5] K.S.Lyalikov and I.B.Razumova-Blyumberg. Chemico-photographic Processes in the Treatment of Cine Films, 30 (1949).

[6] K.S.Lyalikov and V.N.Piskunova. Cinechemicophotographic Industry, 3, 24 (1934).

[7] G.W.W.Stevens, R.G.W.Norrish, Phot.Journal, 78, 11, 513 (1938).

[8] W.Meidinger. Die theoretischen Grundlagen der photographischen Prozesse. 225 (1932).

Received January 15, 1950.

[1]) See Plate, p. 1387

CORROSION OF IRON BY BENZENE SOLUTIONS OF IODINE[1)]

L. G. Gindin and M. V. Pavlova

As in the case of copper and lead studied earlier, iron also showed itself sensitive to benzene solutions of iodine. After only 3-4 days immersion in a solution, samples of iron were covered with a considerable layer of corrosion product.

In experiments with iron (Table 1) we met with such a stoichiometric non-correspondance in the losses of metal and halogen, calculated on the basis of FeI_2, that there appeared to be an extremely peculiar course of the corrosion process in this particular case.

Table 1

Corrosion of Iron by Benzene Solutions of Iodine

Titer of the initial solution 0.0266 g/ml (0.2096 N)

Composition of the iron (in %): C 0.21, P 0.15, Si 0.19, Mn 0.31

Duration (in days)	Quantity of solution (in ml)	Loss of metal (in g)	Iodine reacted (in g)	Iodine reacted (in % on total quantity)	Iodine which should have reacted, calculated from FeI_2	Ratio of reacted to calculated iodine (in %)
50	75	0.6693	0.4875	24.43	3.0419	16.02
	75	0.4586	0.4725	23.69	2.0843	22.67
	70	0.5782	0.6160	33.08	2.6279	23.44
	65	0.3944	0.3250	18.79	1.7925	18.13
	80	0.3890	0.4648	21.37	1.7683	26.29
	75	0.2667	0.3825	19.17	1.2124	31.54

Note: The surface of the plates after removing the corrosion product was dull and pitted.

The deposit on the plate was quite definitely stratified. The products of corrosion which were present in discrete patches, were thoroughly removed by rubbing with a piece of wadding, moistened with alcohol: the solution in the test tubes at the end of the experiment was practically unchanged in volume.

This peculiarity may be provisionally explained by the fact that iron reacts to form "sub halide" compounds, in which several atoms of Fe are present for one atom of iodine; this suggestion seems less probable than that the primary product of corrosion, FeI_2, which is unstable in the air, decomposes in time into iodine and Fe_2O_3. The latter suggestion - of the continuous regeneration of iodine - appears on the other hand very probable. An answer to this question should be given by an analysis of the corrosion products.

These products were dark brown powders, of very low water solubility. The first step in the analysis was to desorb the iodine by extracting it with benzene, until the latter was a pale pink color.

Even after 25 hours' treatment of the powder in a Soxhlet apparatus, the benzene did not remain colorless when used to extract the materials further (so firmly was the adsorbed iodine held by the products of corrosion). Afterwards, the powder was kept in a vacuum desiccator to constant weight and 0.5-0.6 g of it

[1)] Communication X dealing with the corrosion of metal by non-electrolytes.

was dissolved in 150 ml of distilled water, added in small quantities which as they became colored were decanted, a process which was continued until two successive portions were colorless. The solution was filtered into a 250-ml measuring flask through a weighed ashless filter, to which the precipitate was finally transferred. The flask was filled up to the mark and the filter, with the deposit, was dried at room temperature to constant weight. In this way we divided the products of corrosion into fractions soluble and insoluble in water; according to our ideas, the first fraction is mainly ferrous iodide, and the second ferric oxide. We proceeded to analyze them quantitatively.

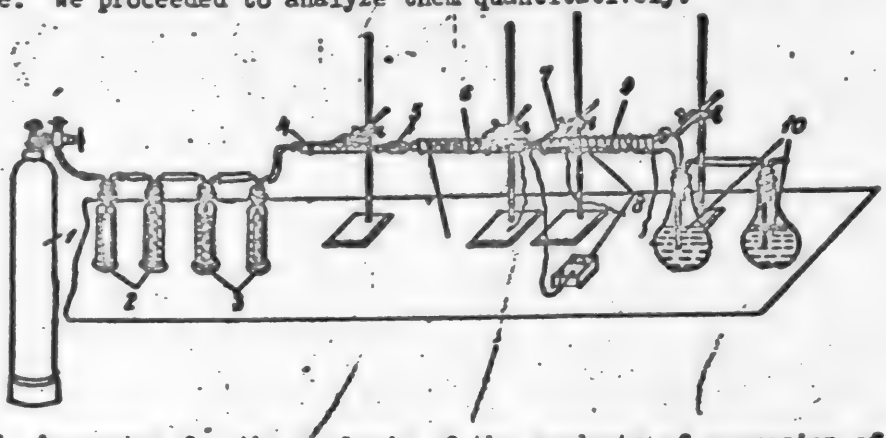


Fig. 1. Apparatus for the analysis of the products of corrosion of iron by iodine. 1) Nitrogen bottles; 2) Dreschel bottles containing alkaline pyrogallol; 3) Dreschel bottles containing H_2SO_4; 4) tubes with solid KOH; 5) tube with glass wool; 6) porcelain tube with nichrome winding filled with copper gauze; 7) pyrex tube with a nichrome winding; 8) thermocouple with millivoltmeter; 9) boat with products of corrosion; 10) receivers containing KI solution.

The solution was analyzed for iron and iodine. The iodine was determined argentometrically, the iron as the hydroxide [1].

The dark brown powder, insoluble in water, was investigated as follows. A porcelain tube with ~0.4g of the powder was placed in a refractory glass tube heated by a nichrome winding, one end of the tube was connected to a drying train with a nitrogen bottle, and the other, conical, dipped into a solution of potassium iodide (Fig. 1). After passing a stream of oxygen-free, dry nitrogen for 30 minutes through the apparatus, the tube was heated to 400-450°, a temperature which was maintained for 40-50 minutes, nitrogen being passed through the tube during the heating. To complete this operation, aimed at separating the oxides of iron from iodine and from traces of iron iodide, which should be volatilized[1] under the conditions described, and absorbing the iodine in potassium iodide, the boat was taken out and weighed, and the tube was carefully washed through with a solution of KI which was added to the solution in the absorbing vessels. Afterwards, the iron and iodine in solution were determined and the substance remaining in the boat was analyzed by X-rays.

The results of all these determinations are set out in Table 2,[2] from which it follows that the corrosion product contained 3-7% of ferrous iodide; the main bulk of these products, not counting the adsorbed iodine, consists of another substance, which, as X-ray examination confirmed, was ferric oxide, Fe_2O_3.

---

1) According to Jackson and Derby [2], FeI_2 easily sublimes in an inert gas atmosphere.

2) Table 2 appears on pages 1304-1305.

It should be noted that the untreated residue, in the state in which it was found on the iron plate, did not give an X-radiogram. Only heating it to 450° in a stream of nitrogen (carefully freed from oxygen) converted it to a state in which it gave an X-radiogram with the interference line characteristic of Fe_2O_3 (Fig. 2a)* and identical with X-radiograms obtained under the same conditions with pure ferric oxide from Kahlbaum (Fig. 2b)*. Evidently, Fe_2O_3 is formed in the amorphous condition. In the process of heating it crystallizes, thus causing the lines, characteristic for Fe_2O_3, to appear on the X-radiogram.[1] Such conversions of amorphous oxides to crystalline ones are described in the literature [3].

By analogy with what we found in treating the corrosion of other metals, it is natural to suppose that iron also is subject to the action not only of iodine but also of oxygen, dissolved in the benzene and to a known extent penetrating in from the atmosphere. In such a case Fe_2O_3 can frequently appear as a product of the direct action of oxygen on iron. However, Fe_2O_3 should be regarded mainly as a product of secondary attack, formed as a result of the decomposition of ferrous iodide. The high sensitivity of FeI_2 to oxygen and its ability to be gradually converted, even at room temperature, to Fe_2O_3 is well documented, particularly in the work of Jackson and Derby already mentioned [2]. On account of the very important role of oxygen thus revealed, it appeared of interest to investigate the action of a solution of iodine on iron in an atmosphere of inert gas. In such an atmosphere, the corrosional process should not be so extensive and the ferrous iodide formed should remain unchanged.

To achieve this, a series of experiments were carried out (Table 3) in closed tubes filled with nitrogen. Plates of iron were placed in a glass tube, after which the tube was drawn down and closed with a rubber bung, carrying 2 stopcocks, one of which was connected to a forevacuum pump and the other to a bottle containing the benzene solution of iodine, connected in turn with a nitrogen bottle; a stream of nitrogen was previously passed through the solution to eliminate air. By turning the taps in the proper way, the tube was first evacuated and then filled with a solution of iodine; then it was sealed off.

Table 3

Corrosion of Iron by a Benzene Solution of Iodine in an Atmosphere of Nitrogen
Titer of the Initial Solution 0.0285 g/ml (0.2244 N)

Duration of the experiment (in months)	Quantity of solution (in ml)	Loss of metal (in g)	Reacted Iodine (in g)	Reacted Iodine (in % of total quantity)	Amount which should have reacted, calculated from FeI_2	Ratio of reacted to calculated iodine (in %)
20	40	0.0864	0.3920	34.38	0.3925	99.80
		0.0767	0.3440	30.18	0.3486	98.68
		0.0759	0.3440	30.18	0.3451	99.68
		0.0704	0.3160	27.72	0.3199	98.79

Note: The surface of the plate, on removing the corrosion product, was clean and lustrous.

In contrast to those obtained in air, the corrosion products in an atmosphere of nitrogen almost completely dissolved in water.[2]

[1]) The X-radiographic investigation of the corrosion products was carried out at our request by E.M.Levitskim, to whom we convey our thanks.

[2]) Only a very fine deposit remained on the filter on filtering the solution. On burning off the filter a trace of Fe_2O_3 on the floor of the crucible was found, and during the operation some iodine vapor came off.

*) See Plate, p. 1387

Table 2

Analysis of Corrosion Products of Iron

Initial Weight (in g)	Fraction I, insoluble in water						
	Weight of fraction (in g)	Weight of residue in porcelain boat (in g)	Weight of iodine absorbed by KI (in g)	Weight of iron contained in the KI solution (in g)	Total weight of components of fraction I (in g)	% on weight of fraction	Deficit (in % of original weight)
0.4673	0.4010	0.2736	0.1254	Not found	0.3990	99.50	0.50
0.5210	0.4378	0.2985	0.1386		0.4371	99.83	0.17
0.4812	0.4410	0.2896	0.1492		0.4388	99.50	0.50

Note: The excess of iodine in fraction II, compared with the iron, is due to the molecular iodine dissolved in an aqueous solution of FeI_2. The calculation of FeI_2 was made on the basis of figures for the content of Fe in Fraction II. For the weight of Fe_2O_3 the weight of the residue in the porcelain boat was taken.

Judged by the results of analysis (Table 4) pure ferrous iodide was present in the aqueous solution. This confirms the supposition that the primary product of corrosion of iron is FeI_2, which decomposes under the influence of oxygen into iodine and Fe_2O_3.

The experiments described lead us also to think how prejudicial for iron was the transformation of FeI_2 into Fe_2O_3. Judged by the fact that, in 20 months in an atmosphere of nitrogen, iron corroded so very much less than in 50 days in the atmosphere containing oxygen, it can be concluded that the layer of ferrous iodide formed was in a state to protect the iron completely from the iodine. However the layer ceased to be protected when the FeI_2 began to suffer decomposition, involving a breakdown of its previous homogeneous and compact structure. It must also be borne in mind that conversion of FeI_2 is accompanied by a liberation of iodine, which ensures its re-circulation and increases its catalytic character; if the reserves of iodine in solution are also partially exhausted, this is mainly by adsorption on Fe_2O_3.

Table 4

Analysis of Corrosion Products of Iron by Benzene Solutions of Iodine in an Atmosphere of Nitrogen

Found (in g)		Iodine that should be present, calculated on FeI_2	Ratio of found to theoretical iodine (in %)
Fe	I		
0.0118	0.0535	0.0536	99.81
0.0118	0.0540		100.74
0.0150	0.0676	0.0682	99.12
0.0150	0.0678		99.41

Thus, in the presence of oxygen, iodine is continuously regenerated, facilitating the conversion of large quantities of iron, through FeI_2, to Fe_2O_3.

The question of the corrosion of metals by solutions of iodine is an extremely interesting one, requiring further study. It would be desirable in the first instance to find out how these solutions act on other metals, and what are the differences in behavior of iodine dissolved in aliphatic, aromatic and other hydrocarbons.

SUMMARY

It has been established that the primary product of the corrosion of iron in benzene solutions of iodine is FeI_2, which is converted to Fe_2O_3 by oxygen; this conversion stimulates the corrosion and is accompanied by the liberation of iodine,

Table 2

Fraction II, soluble in water						$\frac{FeI_2}{Fe_2O_3 + FeI_2}$ (in %)	Total weight of the components of Fracs. I and II		Deficit in % of original weight
Weight of fraction (in g)	Weight of iodine (in g)	Weight of iron (in g)	Total weight (in g)	Total weight % on weight of fraction	Deficit (in %)		(in g)	(in % of orig. weight)	
0.0663	0.0595	0.0035	0.0630	95.03	4.97	6.62	0.4640	99.29	0.71
0.0832	0.0762	0.0017	0.0779	93.63	6.37	3.05	0.5150	98.85	1.15
0.0402	0.0354	0.0020	0.0374	93.04	6.96	3.62	0.4762	98.96	1.04

which gives the solutions an aggressiveness which is continuously regenerated.

LITERATURE CITED

[1] I.M.Kolthoff and E.V.Sendel. Quantitative Analysis (Russian translation). Moscow, 276, 282 (1941).

[2] C. L. Jackson and H. Derby, Am.Chem.J., XXIV, 15 (1900).

[3] I. R. Katz. X-Radiography of Colloids and Textiles (Russian translation). United Sci.Tech.Press, 258 (1937).

Received May 10, 1950

BLANK
PAGE

CONTROL OF OPERATION OF MIXING VESSELS WITH CONTINUOUS FLOW OF REAGENTS UNDERGOING A FIRST ORDER REACTION

B. N. Devyamov and G. N. Bogachov
Laboratory of Mineral Salts UNIKHIM

For the practical execution of reactions continuously, in a series of mixing vessels, it is essential to know the factors which determine the course of the process. Papers dealing with the theory of continuous processes, [1,2,3,4,5] do not deal with the question of their control when they are subjected to some disturbing influences. We take the task of control to be to restore the concentrations of the reagents, which have been changed by some disturbing influence, to their previous value, and to achieve this as quickly as possible and to maintain it there with the least possible deviation from this concentration.

The transition process of establishing the concentration of the reacting substances. In our previous work [6], a method of determining the fraction of reacted substance (D), in the flow passing through a chain of stirring vessels, as a function of time [D = D(t)] was given. If the time of working of the mixer increases without limit, then the value of the fraction of reacted substance (D) reaches a stable limiting value, and determines the concentration of the reagents. However, during the period of transition this does not occur, because in addition to the reaction there is also the process of displacing the liquid filling the reacting space initially.

Hence the first task of our investigation is to find the expression for the build-up process of establishing the concentration of the reacting substances.

If we imagine one mixer with a continuous flow and divide it into elementary volumes, the changes in which we can follow as a function of time, the lowering of the concentration as the result of reaction in the time from t_1 to t_2 can be expressed in the following form:

$$\frac{C_0[v_2 D(t_2) - v_1 D(t_1)]}{V_2 - V_1} \qquad (1)$$

where C_0 is the initial concentration of the reacting substance; V_1, V_2 are the volumes at the moments of time t_1, t_2; $D(t_2)$ and $D(t_1)$ are the fractions of reacted substance at the instants of time t_2 and t_1. Replacing the volume by the expression $V = F(t)$, where F is the volumetric rate of flow, and replacing V by $V + \Delta V$ and t_2 by $t + \Delta t$, Expression (1) may be written as follows:

$$\frac{C_0 t[D(t) + \Delta t) - D(t)]}{\Delta t} + \frac{C_0[\Delta t D(t + \Delta t)]}{\Delta t} \qquad (2)$$

which, taken to the limit becomes

$$C_0[tD'(t) + D(t)] = C_0[tD(t)]' \qquad (3)$$

Expression (3) gives (in general form) the lowering of concentration of the substance at the instant of time t as a result of the reaction.

Inserting the value of D(t) obtained earlier [6] in this expression, we get

$$[tD(t)]' = \frac{1}{\frac{F}{vK_1} + 1} \left[1 - e^{-\left(\frac{F}{v} + K_1\right)t}\right] \qquad (4)$$

where F is the rate of flow of the reagents (L^3/T); v is the working space of the mixer (L^3); K_1 is the rate constant for a first order reaction (1/T). If we put

$$\frac{1}{K_1\left(\frac{F}{vK_1} + 1\right)} = \tau \qquad (5)$$

then Equation (4) may be written thus:

$$[tD(t)]' = K_1\tau\left[1 - e^{-\frac{t}{\tau}}\right] \qquad (4a)$$

The change of the concentration of the original substance with time may be here expressed in the following form:

$$C_n = C_0 - C_0K_1\tau\left(1 - e^{-\frac{t}{\tau}}\right)$$

or, otherwise, in the form of the operator W(P)[1] as the difference between the two operators $W_1(P) = 1$ and $W_2(P) = \frac{K_1\tau}{1 + \tau P}$.

Hence we find:

$$W(P) = 1 - \frac{K_1\tau}{1 + \tau P} = (1 - K_1\tau)\,\frac{1 + \frac{\tau}{1 - K_1\tau}P}{1 + \tau P} = \frac{F}{F + vK_1} \cdot \frac{1 + \frac{v}{F}P}{1 + \tau P} = \frac{1}{1 + K_1\theta} \cdot \frac{1 + \theta P}{1 + \tau P}$$ [2]

where $\theta = \frac{v}{F}$.

If dilution alone is taken into account, then the concentration in the mixer, as can easily be shown, will change in exponential fashion:

$$C_n = C_0\left(1 - e^{-\frac{F}{v}t}\right)$$

This change is characterized by the operator

$$W_3(P) = \frac{1}{1 + \frac{v}{F}P}.$$

Thus neither of the operators W(P) and $W_3(P)$ depend on the concentration, so that the resulting operator of the system consists of the products of reaction and dilution operators:

$$\bar{W}(P) = W(P) \cdot W_3(P) = \frac{1}{1 + K_1\theta} \cdot \frac{1}{1 + \tau P}$$

---

1) $P = \frac{d}{dt}$ – the differentiation operator.

2) After this paper had been written a paper appeared in Ind. Eng. Chem. [7] also dealing with the working of chains of mixers, and using operational calculus.

For n mixers, evidently, we have:

$$W_n(P) = \left(\frac{1}{1 + K_1\theta}\right)^n \cdot \frac{1}{(1 + \tau P)^n} .$$

For unit impulsive disturbance of the system (a sudden change of C_0 equal to unity), to this operator, as we know from operational calculus, corresponds the transition process:

$$C_n(t) = C_0 \left(\frac{1}{1 + K_1\theta}\right)^n \cdot \left[1 - \left(1 + at + \frac{a^2t^2}{1\cdot 2} + \cdots + \frac{a^{n-1}\,t^{n-1}}{(n-1)!}\right) \cdot e^{-at}\right], \quad (6)$$

where

$$a = \frac{1}{\tau} = K_1\left(1 + \frac{1}{K_1\vartheta}\right).$$

Formula (6) gives the change of concentration in the transition (build-up) process on leaving a chain of n stirrers. From the point of view of regulation, this expression may be conceived of in the form of a curve for a self-regulating system. For an unlimited increase in the time we have:

$$\lim_{t \to \infty} C_n(t) = C_n = C_0 \left(\frac{1}{1 + K_1\theta}\right)^n , \quad (6a)$$

i.e. the expression, derived for an established process in all works dealing with the theory of operation of chains of mixers [1,2,3,4,5]. It should be mentioned that Kirillov [1] obtained Expression (6) by inductive means, and the formula was obtained by using operational calculus in the paper by Muson and Pirt [7].

Dependence of the build-up process on the parameters of the system. The second problem in this investigation was the description of the dependence of the transition process in the system on its parameters. This may enable systems to be selected having the best combinations of properties, taking into account the qualitative characteristics of the build-up process for unit impulsive disturbance of a non-regulated system. The quality of the transition process, relative to the newly established regime, may be evaluated, as is usually done in the theory of errors [8,9,10], as the integral sum of the squared deviations. This may be written as follows

$$I_n = \int_0^\infty \alpha^2 dt = \left(\frac{1}{1 + K_1\theta}\right)^{2n} \cdot \int_0^\infty \left(1 + at + \frac{a^2t^2}{2!} + \cdots + \frac{a^{n-1}\,t^{n-1}}{(n-1)!}\right)^2 \cdot e^{-2at} \cdot$$

$$\cdot\, dt^{1)} = \left(\frac{1}{1 + K_1\theta}\right)^{2n} \cdot \left\{ - \frac{e^{-2at}}{2a} \sum_{m=0}^{2(n-1)} \left[\frac{\left(1 + at + \cdots + \frac{a^{n-1}\,t^{n-1}}{(n-1)!}\right)^2}{(2a)^m}\right]^{(m)} \right\}\Bigg|_0^\infty , \quad (7)$$

where I_n is the sum of the squares of the deviations; α is the deviation. The optimum regime in this sense corresponds to a minimum of the Integral (7). The values of the latter for n = 1,2,3,4, and 5 mixers in a chain are set forth in Table 1. The relation for a larger number of mixers was not investigated, because I_n then changes very little.

Supposing that in different systems, of equal total volume, the efflux is at a constant (established) concentration, i.e.

$$\left(\frac{F}{F + VK_1}\right)^n = \left(\frac{1}{1 + K_1\theta}\right)^n = A_2 = \text{const},$$

and $$yn = V = \text{const}, \quad (8)$$

where y is the working volume of each separate mixing vessel; n is the number of vessels, V is the total volume of the chain of mixers. We thus obtain

[1]) See [11].

$$\frac{x}{F} = \theta = \frac{1 - \sqrt[n]{A_2}}{K_1 \sqrt[n]{A_2}} \qquad (9)$$

Introducing this expression in place of Θ, into Equation (7), we obtain for I_n the series of values given in Table 2, where, in addition, the numeral values of I_n for $A_2 = 0.1$, 0.3, and 0.5 and for $K_1 = 1$ are collected.

These values of I_n are shown graphically in Fig.1. By examination of this we see that for each separate value of A_2, i.e., for each given final concentration of the initial reagents on efflux from the system, the quality of the build-up process deteriorates as the number of mixers increases. With increase of A_2, i.e.with decrease of the consumption of the reagents, the quality of the transition process also deteriorates for a given number of mixers in the chain. It would be a good idea to take other criteria of the quality of the transition process, which would allow for the fact that very large deviations from the newly established regime should have less weight in the criterion, because in this case we have small deviations from the old regime.[1)]

TABLE 1

Values of the Integral I_n for Chains Containing Different Numbers of Mixers

No. mixers in chain, n	General Expression for I_n
1	$\frac{1}{2}\left(\frac{1}{1+K_1\theta}\right)^2 \cdot \left(\frac{\theta}{1+K_1\theta}\right)$
2	$\frac{5}{4}\left(\frac{1}{1+K_1\theta}\right)^4 \cdot \left(\frac{\theta}{1+K_1\theta}\right)$
3	$\frac{33}{16}\left(\frac{1}{1+K_1\theta}\right)^6 \cdot \left(\frac{\theta}{1+K_1\theta}\right)$
4	$\frac{93}{32}\left(\frac{1}{1+K_1\theta}\right)^8 \cdot \left(\frac{\theta}{1+K_1\theta}\right)$
5	$\frac{465}{128}\left(\frac{1}{1+K_1\theta}\right)^{10} \cdot \left(\frac{\theta}{1+K_1\theta}\right)$

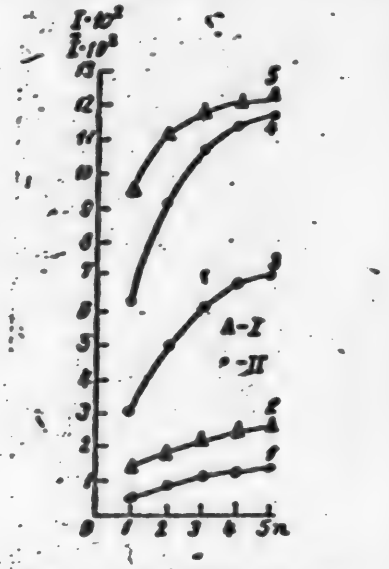


Fig. 1. Quality of the transition process as a function of the number of mixers.

I – I, II – values of I,: 1 and 2-$A_2 = 0.1$; 3 and 5 – $A_2 = 0.3$; 4 – $A_2 = 0.5$.

As such a criterion, the integral sum of the deviations of the square for the transition process from the square for the newly established regime may be taken:

$$I_n = \int_0^\infty [M^2 - (M-\alpha)^2]dt = \int_0^\infty (2M\alpha - \alpha^2)dt = M\int_0^\infty 2\alpha dt - \int_0^\infty \alpha^2 dt = 2M\bar{I}_n - I_n \qquad (10)$$

where M is the value of the established concentration after the disturbance (initial concentration taken as zero); α is the deviation of the concentration from that for the newly established regime in the transition process;

$$\bar{\bar{I}} = \int_0^\infty \alpha dt.$$

[1)] Since during the time of the build-up it is prejudicial to take, in the first place, the external constancy of the concentration, then it is also prejudicial to ascribe the same importance to deviations from the new regime as from the old one. The integral sum of the squares of the deviations from the average values of the concentrations during the time of practical importance of such changes, would constitute the best picture of the quality of the transition process.

Table 2

Value of the Integral I_n, Expressed as the Degree of Consumption of the Initial Substances

No. of mixers in the chain, n	General expression for I_n	Numerical value of I_n for $K_1 = 1$ and and A_2 equal to:		
		0.1	0.3	0.5
1	$\frac{1}{2} A_2^2 \cdot \frac{1-A_2}{K_1}$	0.0045	0.0315	0.0625
2	$\frac{5}{4} A_2^2 \cdot \frac{1-\sqrt{A_2}}{K_1}$	0.0086	0.0508	0.0917
3	$\frac{33}{16} A_2^2 \cdot \frac{1-\sqrt[3]{A_2}}{K_1}$	0.0110	0.0614	0.1060
4	$\frac{93}{32} A_2^2 \cdot \frac{1-\sqrt[4]{A_2}}{K_1}$	0.0125	0.0678	0.1150
5	$\frac{465}{128} A_2^2 \cdot \frac{1-\sqrt[5]{A_2}}{K_1}$	0.0134	0.0702	0.1170

To calculate I it is necessary to find: $\bar{\bar{I}} = \int_0^\infty a\,dt$

$$I = \left(\frac{1}{1 + K_1\theta}\right)^n \int_0^\infty \left(1 + at + \cdots + \frac{a^{n-1} t^{n-1}}{(n-1)!}\right) e^{-at}\,dt = \left(\frac{1}{1 + K_1\theta}\right)^n \cdot \frac{n\theta}{(1 + K_1\theta)} \quad (11)$$

Whence we obtain: $\bar{I} = 2\left(\frac{1}{1 + K_1\theta}\right)^{2n} \cdot \frac{n\theta}{(1 + K_1\theta)}$ — $I = 2A_2^2 \cdot \frac{n}{K_1} \cdot \left(1 - \sqrt[n]{A_2}\right) - I. \quad (12)$

Table 3

Value of the Integral I_n, Expressed as the Degree of Consumption of the Initial Reagents

No. of mixers in the chain, n	General expression for I_n	Numerical value of I_n for $K_1 = 1$ and A_2 equal to:		
		0.1	0.3	0.5
1	$\frac{3}{2} A_2^2 \cdot \frac{1}{K_1}(1-A_2)$	0.0135	0.0945	0.188
2	$\frac{11}{4} A_2^2 \cdot \frac{1}{K_1}(1-\sqrt{A_2})$	0.0188	0.1120	0.199
3	$\frac{63}{16} A_2^2 \cdot \frac{1}{K_1}(1-\sqrt[3]{A_2})$	0.0211	0.1170	0.202
4	$\frac{163}{32} A_2^2 \cdot \frac{1}{K_1}(1-\sqrt[4]{A_2})$	0.0235	0.1190	0.203
5	$\frac{815}{128} A_2^2 \cdot \frac{1}{K_1}(1-\sqrt[5]{A_2})$	0.0250	0.1230	0.205

Inserting I_n in this expression, and making the calculation for the case of $A_2 = 0.1$, 0.3, and 0.5, and for $K_1 = 1$, we get the values of I_n, collected in Table 3.

The functional character $\bar{I}_n$ (n) (fig.1) is the same as for I_n. Thus, the family of curves for I_n and for $\bar{I}_n$ (fig. 1) shows the change in the quality of the transition process as the number of mixers n increases.

From the form of these curves, the desirability of selecting one or the other parameters of the system can be decided if, of course, at the same time we bear in mind the character of the change of the other properties of the system. For example, it should be considered that a deterioration of the quality of the transition process as n increases would correspond to a decrease in the total volume of the mixers, required to attain a given value of A_2. The requirement of attaining A_2 may be met, for example, by setting a definite productivity A for the chain of mixers.

Let us now make the requirement that the productivity of the chain be kept constant with a given number of mixers n.

In this case: $(1 - A_2)F = A = \text{const}$ and $\frac{V}{n} = V = \text{const}$.

whence: $$F = \frac{A}{1 - A_2} \quad \text{and since} \quad \frac{V}{n} = \frac{V}{n} \quad \text{and} \quad A_2 = \left(\frac{1}{1 + K_1\theta}\right)^n$$

we obtain finally:

$$A = \sqrt[n]{A_2}\left[A - \frac{V(1 - A_2)K_1}{n}\right] \qquad (13)$$

It can be seen without difficulty that for this case it is natural to use as a criterion the minimum-ness of the integral sum $M \int_0^\infty \alpha dt$ (product of the integral of the deviations of the parameter from the new regime and the value of the parameter for this newly established regime). Whence we find:

$$Z = M \int_0^\infty \alpha dt = A_2^2 \frac{n}{K_1}\left(1 - \sqrt[n]{A_2}\right) = Z(n), \qquad (14)$$

in which A_2, for insertion in Expression 14, is found from Equation (13) for a given value of n. Taking two values of A = 0.5 and 1.5, and calculating the corresponding values of A_2 for different values of n(1,2,3,4, and 5 mixers in the chain) and different values of V(2,3), again for $K_1 = 1$, the results are summarized in Table 4.

Table 4

Values of the Final Concentration A_2

No. of mixers in the chain, n	V	Value of A_2 for A equal to: 0.5	1.5
1	2	0.167	0.750
	3		
2	2	0.069	0.677
	3		
3	2	0.039	0.658
	3		
4	2	0.028	0.642
	3		
5	2	0.021	0.624
	3		

Determining Z as well, we obtain the values shown in Fig.5, from which we see that in the first case Z(n) grows and in the second case it falls.

Thus by changing the various parameters of the system we can get different families of curves, completely characterizing the chain of mixers. Thus we can always get the necessary information relative to the

selection of the parameters of the system, which will ensure the optimum running of the process, taking into account the output of the apparatus, the values of the parameters for the stationary state, and also the form of the transition process.

Table 5

Values of Z for Different Conditions

No. of mixers in the chain, n	1	2	3	4
Values of Z for V = 2, A = 1.5	0.140	0.164	0.169	0.181
Values of Z for V = 3, A = 0.5	0.0233	0.0068	0.003	0.00184

Determination of the attainable controllability of the system as a function of the parameters. As a characteristic of the controllability of the system to be regulated we take the quality of regulation provided by a simple automatic regulator, without reverse connections, and with the best construction i.e. with the optimum coefficient of amplification K_0 of the regulator.

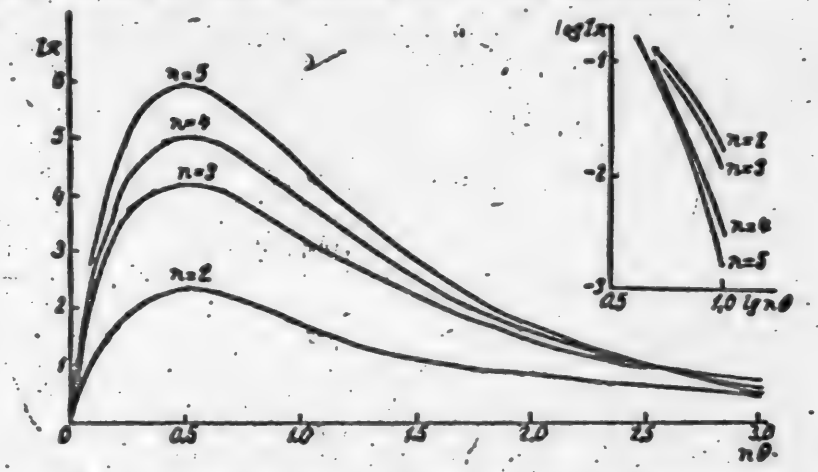


Fig.2. Characteristic of the quality of regulation

In defining the concept of the quality of regulation, two factors should naturally be borne in mind: 1) the value of the deviation of the parameter from the nominal during the transition period; and 2) the time during which this deviation persists. The quality of the transition process will be characterized by the value of $I = \int \rho^2(t)dt$ [8,9,10,12]. This value is conceived as the sum of the squared deviations from nominal during the transition process, caused by unit sudden disturbance of the process on entry, during the working of a simple regulator without reverse connections and with the best construction.[1] Such a criterion of the deviation of the curve expressing the change of parameters during the transition process[2] is apparently, the most suitable one [8,9,10,12].

[1] The best construction is attained by a corresponding choice of amplification coefficient K_0 of the regulator.

[2] Approximation of the function by the method of least squares.

Frequency analysis [13,14] enables the form of the function $I = I(n, n\theta)$ to be determined graphically. For our case it is represented in Fig.2 from the data in Table 6.

Table 6

No. of mixers n	nθ													
	1/100	1/10	1/8	1/5	1/4	3/8	1/2	3/4	1	1 1/2	2	3	5	10
2	0.141	1.13	1.334	1.325	2.02	2.29	2.378	2.21	1.91	1.325	0.95	0.4	0.137	0.0187
3	0.235	1.94	2.29	3.10	3.47	4.00	4.13	3.83	3.22	2.14	1.36	0.57	0.127	0.008
4	0.283	2.32	2.75	3.73	4.18	4.86	5.01	4.63	3.90	2.47	1.51	0.57	0.097	0.003
5	0.331	2.72	3.22	4.39	4.93	5.71	5.91	5.46	4.55	2.82	1.67	0.56	0.082	0.002

On the basis of the above mentioned calculations, the following considerations are put forward. Using the frequency method [13], we find that

$$\varphi(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \left[\frac{1}{\sqrt{2\pi}} \cdot \frac{1}{(-jq)} \cdot \frac{W_n(-jq)}{1 + K(-jq)} \right] e^{-jqt}\, dq ,$$

where $W_n(P)$ is the object operator (system of mixers); $K(P)$ the coefficient of amplification of the regulated system, with the regulator in the disengaged position,

$$K(P) = W_n(P) \cdot \frac{K_0}{P}$$

Whence, using the Parseval equality for the Fourier integral [15], we obtain:

$$\int_{-\infty}^{+\infty} |\varphi(t)|^2 dt = \int_{-\infty}^{+\infty} \left| \frac{1}{\sqrt{2\pi}} \cdot \frac{1}{(-jq)} \cdot \frac{W_n(-jq)}{1 + K(-jq)} \right|^2 dq = \frac{1}{\pi} \int_0^{\infty} \frac{1}{q^2} \left| \frac{W_n(-jq)}{1 + K(-jq)} \right|^2 dq$$

and, since

$$\int_{-\infty}^{0} |\varphi(t)|^2 dt = 0$$

then

$$I = \int_0^{\infty} |\varphi(t)|^2 dt = \frac{1}{\pi} \int_0^{\infty} \frac{1}{q^2} \left| \frac{W_n(-jq)}{1 + K(-jq)} \right|^2 dq$$

but we obtained an expression for the operator object (mixer system).

$$W_n(P) = \left(\frac{1}{1 + K_1\theta} \right)^n \cdot \frac{1}{(1 + \tau P)^n}$$

Whence we find also $I = I(n, n\theta)$.
Making the calculation of the integral graphically,[1] selecting K_0 in each case so that the least value of I is obtained, we arrive at the results set forth in Table 6.

For a single mixer ($n = 1$) $I = 0$, but $K_0 = \infty$, which cannot be attained in practice. With $K_0 \neq \infty$ we get $I \neq 0$ depending on the value of K_0. Thus the picture is complicated considerably. The principal papers dealing with the case of a single mixer are useless [1,2,3,4,5], since they pass over this case.

In the upper right corner of Fig.2, part of the curve in the region of large values of nθ has been plotted on a logarithmic scale. We see that, beginning with certain values of nθ, the order of succession of the curves changes.

By comparing the transition processes it can be shown that, although they occur with satisfactory I values (areas) the rate of change of the deviation is

[1] The method determining the numerical values of the integral I was proposed by L. A. Kostromitin.

very large in the whole transition process. [$\dot{\varphi}(t)$ large] which is a negative factor in regulation [16]. Therefore we made the calculation of the criterion

$$\bar{I} = \int_0^\infty [\varphi^2(t) + \dot{\varphi}^2(t)]\,dt$$

which also takes into consideration the rate of change of the parameter.

$$\bar{I} = \int_0^\infty [\varphi^2(t) + \dot{\varphi}^2(t)]dt = \int_0^\infty \varphi^2(t)dt + \int_0^\infty \dot{\varphi}^2(t)dt = I + \tilde{I}.$$

$\tilde{I}$ is obtained, analogous to I, by simple addition of the integral differentiated with respect to the parameter t.

$$\tilde{I} = \int_0^\infty |\dot{\varphi}(t)|^2 dt = \frac{1}{\pi}\int_0^\infty \left|\frac{W_n(-jq)}{1 + K(-jq)}\right|^2 dq$$

whence

$$\bar{I} = I + \tilde{I} = \frac{1}{\pi}\int_0^\infty \frac{(1 + q^2)}{q^2} \cdot \left|\frac{W_n(-jq)}{1 + K(-jq)}\right|^2 dq.$$

An analogous calculation was carried out, from which the values of $\bar{I}\theta$ were obtained, collected in Table 7 and represented graphically in Fig.3.

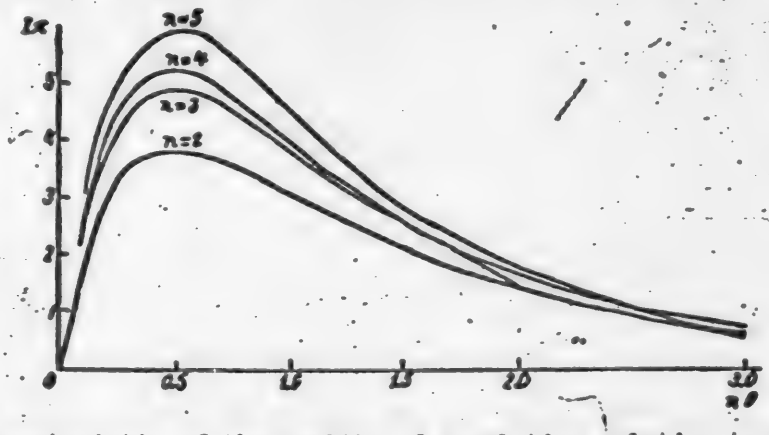


Fig.3. Characteristic of the quality of regulation relative to the rate of change of the process.

Table 7

No. of mixers n	nθ													
	1/100	1/10	1/8	1/5	1/4	3/8	1/2	3/4	1	1 1/2	2	3	5	10
2	0.225	1.80	2.12	2.87	3.21	3.66	3.79	3.53	3.04	2.11	1.44	0.64	0.219	0.03
3	0.278	2.30	2.72	3.68	4.12	4.74	4.89	4.54	3.81	2.53	1.61	0.67	0.150	0.01
4	0.293	2.40	2.84	3.86	4.32	5.03	5.18	4.79	4.03	2.56	1.56	0.59	0.100	0.004
5	0.331	2.72	3.22	4.39	4.93	5.71	5.91	5.46	4.55	2.82	1.67	0.57	0.082	0.002

We see that, accounting for $\dot{\varphi}(t)$ does not considerably change the picture of the variation of quality of the transition process: consequently, for simplicity one can be completely guided by the results obtained for I.

SUMMARY

1. It has been shown that by using operational calculus, and the ideas given earlier [6], an expression for the change of concentration of the substance in any mixer chain may be derived.

2. Some critical values of $K_1 n\delta$ (in our example equal to $\frac{1}{2}$) have been found, for which the control of the operation of the chain of mixers is most difficult. With increase in $n\theta$ the control becomes easier (since at high degrees of exploitation of the substance and with long times of residence, θ, the variations in the supply of reacting mass do not affect matters much). Likewise, with diminution of $K_1 n\theta$ from the critical value, the control is facilitated (in the given case, thanks to a lower degree of exploitation of the reagent, fluctuations in the feed of the reacting mixture do not have much effect).

3. Starting from certain values of $n\theta$ (in our example about 1.5) the change of $n\theta$ has little effect on the quality of the control. However, at some sufficiently large values of $n\theta$, a change in the character of the dependance of the quality of control on n (cf. Fig.2 inset in logarithmic co-ordinates) is produced. At this point the control of the operation of chains of mixers is rendered easier as the number of mixers increases, other conditions being equal, in contrast to the inverse dependence at small values of $n\theta$.

4. Between the direct and inverse dependence of the attainable quality of the optimum control there is an interval of values of $n\theta$, in which the quality changes little as the number of mixers n changes (cf. Fig.2).

5. It has been shown that, by applying operational analysis to the working of mixer chains, concrete problems concerned with the selection of the optimum parameters of the system to get the best regulation of the system can be solved.

LITERATURE CITED

[1] N. I. Kirillov, J. Appl. Chem. 13, 7, 978-1002 (1940).

[2] A. N. Planovsky, 5, 5 (1944) J. Chem. Ind. 6, 5 (1944).

[3] K. N. Shabalin and S. F. Krylov, J. Chem. Ind., 10-11, 4 (1944).

[4] R. B. McMullin and M. Waber. Trans. Amer. Inst.of Chem. Eng., XXXI, 409 (1934-1935).

[5] K. G. Denbig, Trans. Farraday Soc., 40, 352 (1944).

[6] G. N. Bogachov and B. N. Devyatov, J. Appl. Chem. 22, 9, 921 (1949).

[7] D. R. Muson and E. R. Pirt, Ind. Eng. Chem., 42, 817 (1950).

[8] A. N. Krylov, Lectures on approximate calculations, Acad.Sci. USSR 1933.

[9] U. Whittaker and G. Robinson, Mathematical Treatment of Observational Results GTTI (1933).

[10] V. L. Goncharov, Theory of Interpolation and Approximation Functions, United Sci. Tech. Press, (1934).

[11] Ryzhik, Tables of Integrals, Sum, Series and Products. State Tech. Press (1943).

[12] I. P. Natanson, Constructive Theory of Functions. State Tech. Press (1949).

[13] V. V. Solodovnikov, Automatic and Telemechanics, 2, 65-88 (1947); ibid 1, (1946).

[14] Oldenburg and Sartorius, Dynamics of Automatic Regulation, State Energy Press (1949).

[15] Titchmarsh, Introduction to the Theory of Fourier Integrals, State Energy Press (1948).

[16] Feldbaum, Automatics and Telemechanics, I (1948).

Received September 27, 1950.

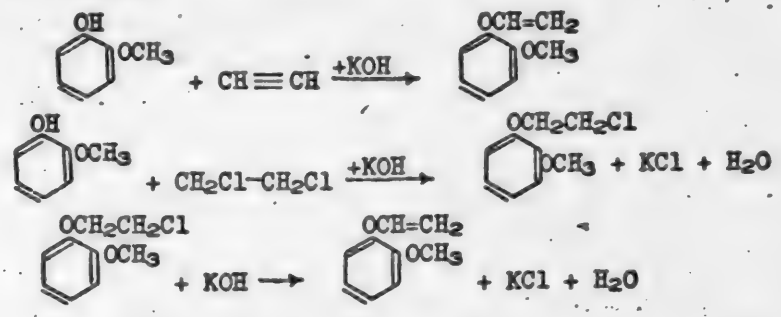
SYNTHESIS OF GUAIACOL VINYL ETHER AND INVESTIGATION OF ITS PROPERTIES

M. F. Shostakovsky, V. P. Shishkov and M. G. Zelenskaya

Laboratory of Vinyl Compounds, Institute of Organic Chemistry,
Academy of Sciences of the USSR

The chemistry of vinyl ethers is one of the new fields of contemporary synthetic organic chemistry. It is interesting to prepare different simple vinyl ethers. At present, the vinylalkyl and partially the vinylaryl ethers have been most studied [1].

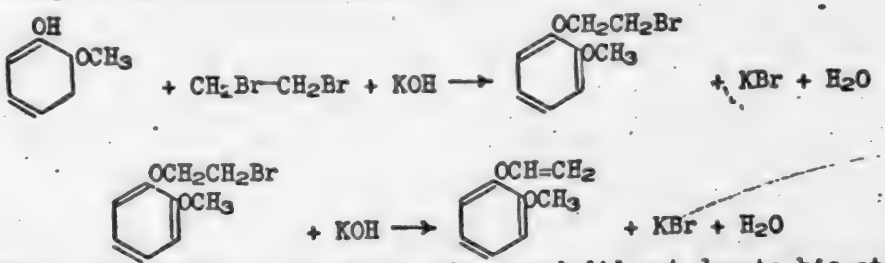
It would be of considerable value to have vinyl ethers of substituted phenols. We undertook the preparation of guaiacol vinyl ether, according to the following two schemes.



The preparation of guaiacol vinyl ether by the action of acetylene on guaiacol in the presence of caustic potash was based on the universal vinylation reaction worked out by Favorsky and Shostakovsky [2].

Another method of obtaining guaiacol vinyl ether is based on the well-known reaction of Butlerov and Eltekov [3].

Berthold was the first to obtain the primary vinyl ether of guaiacol, in 20% yield, according to the following scheme [4]:



This author only prepared the vinyl ether, and did not devote his attention to its chemical properties.

In our work, we started from the more simple and convenient procedure of preparing vinyl ethers by the reaction worked out by Favorsky and Shostakovsky, involving the action of acetylene on compounds containing mobile hydrogen, in the

presence of caustic potash as a catalyst. As a result of the reaction, carried out in an autoclave at 180-200°, the vinyl ether of guaiacol was obtained in more than 60% of the theoretical yield.

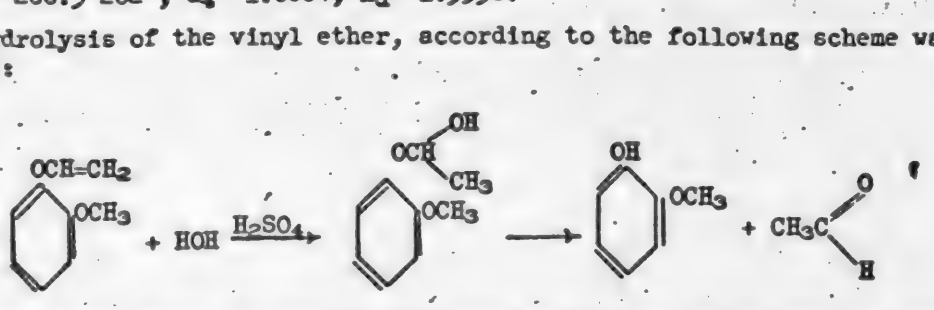
The second point of interest in our work was the preparation of the vinyl ether in two stages. In the first stage guaiacol β-chloroethyl ether was obtained by the action of dichloroethane on guaiacol in the presence of an equimolecular quantity of caustic alkali, followed by the preparation of the vinyl ether itself by the action of caustic alkali on this intermediate chloroethyl ether.

It should be noted that in this reaction, extremely large quantities of alkali are introduced and the ether is obtained in comparatively small yields. Of course, the Favorsky-Shostakovsky method, i. e., direct vinylation by the action of acetylene on guaiacol, is considerably more advantageous and convenient.

Guaiacol vinyl ether prepared was a liquid with the following constants:

B. p. 200.5-202°; d_4^{20} 1.0684; n_d^{20} 1.5356.

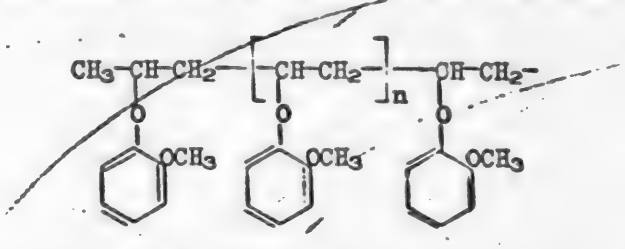
The hydrolysis of the vinyl ether, according to the following scheme was studied [5]:



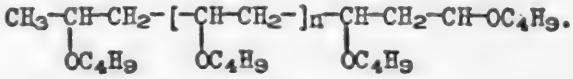
Guaiacol vinyl ether was considerably more stable to hydrolysis by water, in the presence of mineral acids, than vinylalkyl ethers (see Tables 1-4 in the experimental part).

Investigation of the properties of guaiacol vinyl ether established that here the effect of the benzene nucleus is strong; apart from slowing down the hydrolysis, it also caused peculiarities in the formation of an acetal and in polymerization. In general, this ether enters into all reactions characteristic of a simple vinyl ether. The processes of polymerization of guaiacol vinyl ether have not been studied and were not investigated in this work.

We made attempts to polymerize the vinyl ether in the presence of metallic chlorides, from which we would expect the formation of a polymer according to the scheme:



This scheme was proposed on the basis of the observations of Shostakovsky and co-workers, who studied the processes of polymerization of vinylalkyl ethers [5,7]:



The use of guaiacol derivatives is known: "duatol" is a carbon ether of guaiacol [6], and "thiokol" is the potassium salt of orthoguaiacol sulfo acid [7] and finally, "gravitol", has the structure:

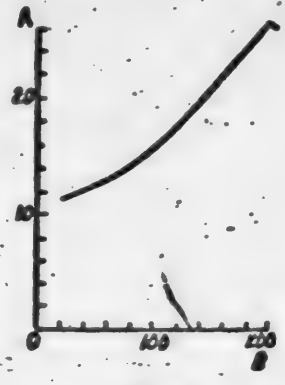
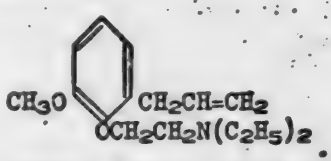


Fig.1.



the latter having found application as an anaesthetic for parturition [8].

In the study of the polymerization of guaiacol vinyl ether, an ionic chain reaction mechanism in the presence of metal chloride was proposed, similar to that obtaining in the polymerization of simple vinyl ethers [9].

It was established that guaiacol vinyl ether did not undergo transformation in the presence of peroxides.

EXPERIMENTAL

Preparation of guaiacol vinyl ether. The preparation of the ether followed the reaction:

$$CH{\equiv}CH + C_6H_4OCH_3OH \xrightarrow{KOH} C_6H_4OCH_3OCH{=}CH_2$$

The reaction was carried out in a rotating stainless steel autoclave with an electrical heating coil (capacity of vessel 2.6 liters). 400 g of guaiacol was charged, along with 80 g of 50% aqueous caustic potash. Acetylene was passed in from a bottle under a pressure of 15 atm, after which the autoclave was heated. In Fig.1 the curves of pressure in the autoclave have been plotted against temperature. The duration of the reaction was 36 hours. The product was a dark colored liquid, which was steam distilled. The distillate was a light yellow liquid which was dried over potash and distilled in vacuum.

The product distilled at 112-113° (30 mm Hg) and came over in one fraction with an extremely small residue in the flask. 257.92 g of the vinyl ether was obtained, 62% of the theoretical yield. The product collected from a number of experiments had the following constants:

B.p. 200.5-202° at 760 mm and 112-113° at 30 mm.
d_4^{20} 1.0648; n_d^{20} 1.5356; MR_D 43.768. $C_9H_{10}O_2$. Calculated MR_D 43.833.

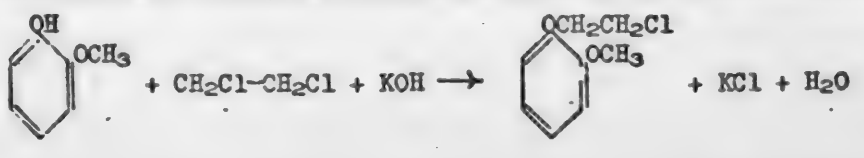
Determination of the molecular weight (cryoscopically):

0.1905 g substance. 20.7 g of benzene, Δt 0.330°. Found: M 143.06. $C_9H_{10}O_2$ Calculated M 150.17.

Microanalytic data

8.515 mg substance: 22.335 mg CO_2; 5.335 mg H_2O; 8.202 mg substance: 21.560 mg CO_2; 5.135 mg H_2O. Found %: C 71.67, 71.71; H 7.01, 7.00. $C_9H_{10}O_2$. Calculated %: C 71.95; H 6.73.

Preparation of guaiacol β-chloroethyl ether. The preparation was as follows:



450 g of dichloroethane, 200 g of guaiacol and 75 g of alkali were charged into a rotating autoclave (2.6 liters). The reaction mass was heated for 10 hours. The temperature of the reaction was 140-150°.

The product was a brown liquid. Dichloroethane was distilled off from the product at atmospheric pressure. The residue was distilled in vacuum.

As a result of the distillation a substance boiling at 140-145° (30 mm) was obtained, pale yellow crystals of m.p. 44°, which was later characterized as guaiacol β-chloroethyl ether.

The yield of the β-chloroethyl ether was 29% of theory, based on the guaiacol taken.

The constants of the β-chloroethyl ether were as follows:

B.p. 250-251°; m.p. 44°.

Microanalytic data

5.708 mg substance: 4.340 mg AgCl; 3.201 mg substance: 2.452 AgCl. Found %: Cl 18.81; 18.95. $C_9H_{11}O_2$. Calculated %: Cl 19.01.

Preparation of guaiacol vinyl ether from the β-chloroethyl ether following the scheme:

$$C_6H_4OCH_3OCH_2CH_2Cl + KOH \longrightarrow C_6H_4OCH_3OCH{=}CH_2 + KCl + H_2O.$$

The reaction was carried out in a three-necked flask, fitted with a stirrer, reflux condenser, thermometer and a dropping funnel.

Into the reaction flask were charged 22 g of β-chloroethyl ether of guaiacol, and 90 ml of ethyl alcohol, and an alcoholic solution of caustic potash (5 g KOH in 80 ml of EtOH) was run in through the dropping funnel.

The reacting mass was heated for 4 hours on a water bath at 80°. On the next day a deposit of potassium chloride was found on the bottom of the flask. The mass was distilled in vacuum. Alcohol distilled over at first, followed by a fraction boiling at 112-113° (30 mm) which was collected. This was the vinyl ether sought; 5 g was obtained. Yield 52% of theory.

The constants of this substance were:

B.p. 112-113° (30 mm); n_d^{20} 1.5357; d_4^{20} 1.0648.

The vinyl ether was hydrolyzed at 60° (Expts. 1 and 2) and 100° (Expts. 3 and 4).

In Expt. No. 1 four closed ampoules, each of 75 ml capacity, containing weighed quantities of the vinyl ether and 10% sulfuric acid, were placed in a thermostat at 60°.

After heating in the thermostat the ampoules were cooled down, and their contents transferred to Erlenmeyer flasks with ground stoppers, after which their acetaldehyde contents were determined by the method devised in our laboratory [10]; in Table 1 the results of the hydrolytic experiments at 60° are set forth.

Expt. No. 2 was carried out under analogous conditions, but using dioxane as a solvent (the vinyl ether does not dissolve in 10% sulfuric acid).

In Table 2 are given the results of the hydrolysis in dioxane at 60°.

Expt. No. 3 was carried out at 100°. Three closed ampoules, each holding 75 ml, containing weighed quantities of the vinyl ether and 10% sulfuric acid, were placed in the thermostat at 100°. Analysis for acetaldehyde after cooling the ampoules was made according to the method worked out in our laboratory. Data about the order of carrying out the experiments and their results are to be found in Table 3.

Table 1

Results of Hydrolysis of Guaiacol Vinyl Ether at 60°

No. of ampoule	Time of heating (in hours)	Weight of vinyl ether (in g)	Quantity of sulfuric acid (in ml)	Quantity of bisulfite (in ml)	Consumption of iodine solution[1] (in ml)		Quantity of vinyl ether determined (in %)
					blank expt.	in test expt.	
1	0.5	0.2167	20	10	21.3	6.5	51.8
2	1.25	0.2098	20	10	21.3	6.1	55.0
3	2	0.2065	20	10	21.3	7.5	50.8
4	6	0.2710	20	10	21.3	4.8	46.2

Table 2

Results of Hydrolysis of Guaiacol Vinyl Ether in Dioxane at 60°

Ampoule No.	Duration of reaction (hrs)	Weight of vinyl ether (g)	Quantity of sulfuric acid (ml)	Quantity of dioxane (ml)	Quantity of bisulfite (ml)	Consumption of iodine solution (ml)		Quantity of guaiacol vinyl ether determined (%)	Notes
						blank expt.	test expt.		
1	0.3	0.1947	20	20	10	18.6	11	29.6	
2	1.5	0.2255	20	20	10	18.6	6.6	40.5	
3	2.5	0.2085	20	20	10	18.6	9.5	33.2	Contents of ampoule pale yellow.
4	4	0.2208	20	20	10	18.6	18.6	–	Contents of ampoule brown

Table 3

Results of the Hydrolysis of Guaiacol Vinyl Ether at 100°

No. of ampoule	Time of heating (hrs)	Weight of vinyl ether (in g)	Quantity of sulfuric acid (ml)	Quantity of bisulfite (ml)	Consumption of iodine solution (ml)		Quantity of vinyl ether determined (in %)
					blank expt.	in test expt.	
1	2	0.2144	20	10	21.8	8.4	47.5
2	4	0.1756	20	10	21.8	13.8	34.6
3	5	0.2051	20	10	21.8	13.2	31.9

Experiment No. 4 was carried out under conditions analogous to those of Expt. No. 3, but using dioxane as solvent. The data about the order of carrying out the experiments and their results are presented in Table 4.

1) The factor of this solution in all experiments was 1.0124.

Table 4

Results of Hydrolysis of Guaiacol Vinyl Ether in Dioxane at 100°

Ampoule No.	Duration of reaction (hrs)	Weight of vinyl ether (g)	Quantity of sulfuric acid (ml)	Quantity of dioxane (ml)	Quantity of bisulfite (ml)	Consumption of iodine solution (ml)		Quantity of guaiacol vinyl ether determined (%)	Notes
						blank expt.	test expt.		
1	0.5	0.1796	20	10	20	20.3	14	26.6	
2	1.5	0.2070	20	10	20	20.3	12.2	29.7	
3	2	0.2185	20	10	20	20.3	17	11.5	Contents of ampoule yellow
4	4	0.2223	20	10	20	20.3	20.3	–	Contents of ampoule brown

Investigation of the tendency of the vinyl ether to polymerize. For the experiments, 10 g of guaiacol vinyl ether and 5 drops of ferric chloride solution were taken. The reaction mixture was placed in a 50 ml flask.

Fig.2 shows how the polymerization reaction proceeds as a function of time at room temperature. As can be seen from this figure, the temperature of the reaction mixture increases rapidly, and 5 minutes after adding the catalyst it is 48°, and then begins to fall slowly.

Since at room temperature the reaction is very slow, the flask with the reaction mixture was placed in a thermostat at 80°. After 3 hours the contents of the flask were a thick, sticky, dark blue mass.

Determination of the Molecular weight (cryoscopically)
0.3465 g substance: 21.85 g benzene; $\Delta t = 0.230°$. Found M 354.1.

SUMMARY

1. Guaiacol vinyl ether has been obtained by vinylating guaiacol in an autoclave at 180-200°, at a maximum pressure of 26-28 atm. The yield was 62% of the theoretical.

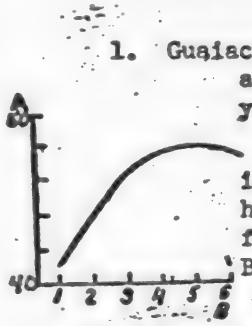


Fig.2.

2. The possibility of obtaining the guaiacol vinyl ether by interaction of sodium or potassium guaiacolate with dichloroethane has been demonstrated. The reaction goes in two stages with the formation of guaiacol β-chloroethyl ether as an intermediate product. Both stages can be telescoped into one by using an excess of alkali.

3. It has been shown that guaiacol vinyl ether hydrolyzes with formation of acetaldehyde, though this process is slower than with vinylalkyl ethers.

LITERATURE CITED

[1] M. F. Shostakovsky and M. S. Burmistrova, J. Appl. Chem. 15, 260 (1942).

[2] A. E. Favorsky and M. F. Shostakovsky, J. Gen. Chem. 13, 1 (1943).

[3] A. M. Butlerov, J. Russ. Chem. Soc., 2, 192 (1870); A.P.Elketov, 9, 163, 357 (1877).

[4] Wohl and Berthold, Ber., 43, 2181 (1910).

[5] A. E. Favorsky and M. F. Shostakovsky, Transactions of the Jubilee Sci. Sess. Leningrad Univ, 1819-1944.

[6] State Pharmacopaeia, 8th Edn., 238 (1946).

[7] State Pharmacopaeia, 8th Edn., 528 (1946).

[8] K. H. Grundriss. Sinthese der modernen Arzneistoff. Stuttgart (1931).

[9] M. F. Shostakovsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. 2, 156 (1943).

[10] M. F. Shostakovsky and E. N. Prilezhaeva, J. Gen. Chem. 17, 1129 (1947).

Received September 30, 1950.

BLANK
PAGE

MECHANISM OF COPOLYMERIZATION OF METHYLMETHACRYLATE WITH ALLYL METHACRYLATE[1)]

B. N. Rutovsky and A. M. Shur

In the majority of published papers on copolymerization, systems of bifunctional monomers have been investigated and in those cases where the copolymerization of tetrafunctional monomers has been studied, the reactions have been carried out under conditions in which only one of the double bonds of the monomer have participated.

The investigation of the copolymerization of systems in which one of the monomers has two active double bonds has therefore considerable theoretical interest.

In our work we have examined, as an example of such a system, the copolymerization of methyl and allyl methacrylates.

EXPERIMENTAL

The initial monomers – allyl methacrylate, methyl methacrylate, and other starting products were obtained and purified in the same way as described earlier [1].

Method of polymerization. The polymerization was carried out in closed ampoules (10 ml) which had previously been cleaned with chromic acid and water, after which they were steamed out and dried. The mixture of monomers of the desired composition, freshly prepared in a stream of nitrogen, was weighed out on an analytical balance, and some benzoyl peroxide (0.5% on the weight of the monomers) was dissolved in it. The mixture was introduced into the ampoules with a micropipette. As rapidly as possible after being filled, the ampoules were immersed in liquid air, and were connected to a tee-piece, connected to a vacuum pump and a source of purified nitrogen. After pumping out to a residual pressure of 2-3 mm Hg, the vacuum line was closed, and the ampoules filled with nitrogen. In this state the contents of the ampoules were thawed out, frozen again and so on. This operation was repeated 2-3 times, after which the ampoules were finally sealed off. The polymerization was conducted in a water thermostat (65 $\pm$ 0.5°), provided with an electrical heater and a stirrer.

After definite intervals of time the ampoules were taken out of the thermostat and rapidly cooled, in order to stop the polymerization. After opening them, the ampoules were connected to weighed U-tubes, immersed in liquid air. The main part of the monomer was driven off at room temperature at a residual pressure of about 1-2 mm: this was continued until a solid product appeared in the ampoule. The last traces of monomer were removed at the same pressure on a water bath, and then on a glycerine bath (150°). Control experiments with a solution of polymer and monomers in the presence of benzoyl peroxide showed that the monomer distilled over practically quantitatively and did not condense further. The whole process usually took about 6 hours, and was considered at an end when the weight of the ampoule did not change appreciably between two successive weighings (no change in the third place). The yield of polymer was determined from the weight of monomer which distilled over. The composition of the copolymer was determined from the analysis of the composition of the monomers, as has already been described [2].

---

1) Communication III dealing with the copolymerization of methyl methacrylate with complex esters of unsaturated alcohols and methacrylic acid.

As our experiments showed, in the initial stages of the copolymerization of allyl and methyl methacrylates, products soluble in organic solvents were formed, which were converted by further polymerization into insoluble ones.

To elucidate the mechanism of this transition we separated the soluble products from the reaction mixture, and investigated the kinetics of formation of the soluble and insoluble polymers.

The polymerization was carried out with a mixture containing 10% (by weight) of allyl methacrylate, since with higher contents of the allyl ester the quantity of soluble polymer was very small, even in the initial stages of the process.

To study the kinetics, ampoules containing a mixture of the monomers with 0.5% of benzoyl peroxide were taken out hourly one at a time, and their contents diluted with dichloroethane. The soluble part of the copolymer was extracted from the ampoules, and the residue was washed out twice with the solvent.

The polymer was thrown out of solution with methanol, filtered off and reprecipitated from dichloroethane with methanol. The polymer, filtered off, was dried to constant weight in vacuum at 65° and weighed. The insoluble, residual gelatinous-looking mass, was extracted from the ampoules, washed with dichloroethane on the filter, extracted 2-3 times with dichloroethane and dried to constant weight together with the soluble polymer. The polymer dissolved in the extract was united with the soluble polymer.

Investigation of the initially soluble polymer. This material was fractionated from 1% solution of the polymer in dichloroethane, and the solution obtained was divided into 10 ml portions. To the first, 1 ml methanol was added with shaking until a turbidity appeared. To the second 10 ml, 1 ml of methanol more was added than to the first, and to the 3rd, 2 ml more than to the first, and so on, so long as addition of methanol caused precipitation of the polymer.

The filtered precipitate was washed on the filter with a mixture of dichloroethane and methanol, taking solvent and precipitant in the same ratio in which they were found at the point of complete precipitation of the polymer. The precipitates were dried at 65° in vacuum to constant weight.

In parallel, the viscosity (in benzene) of the solutions of the initially soluble copolymer and polymers of methyl methacrylate was determined. The latter was obtained under the same conditions as the initial copolymer. Initially 4% solutions were prepared, and after their viscosity had been determined, they were diluted to 2%, then to 1% and finally to 0.5%. The determinations were made in a Ostwald viscosimeter with a capillary of 1 mm diameter; the temperature of the measurement was 20°. The average of five determinations was taken.

The copolymerization was carried out with 10, 50 and 75% of allyl methacrylate in the original mixture. The results of the analysis for a series of experiments are set out in Table 1, where A_o and M_o are the initial quantities of allyl and methyl methacrylates; A and M are the quantities of these esters obtained on distillation. As is shown by the results in Table 1, in the initial stages of the copolymerization, when the percentage conversion does not exceed 20%, the copolymer is richer in allyl methacrylate than is the original mixture. At later stages of the process, on the other hand, the copolymer becomes poorer in allyl methacrylate than the original mixture. Apart from this, while in Expts. Nos. 2,4 and 6 the separation of an insoluble gel from the reaction mixture was observed, in Expts. Nos. 1,3 and 5 the system remained fairly homogenous throughout.

The result of the investigations of the kinetics of the formation of soluble and insoluble copolymers is shown in Table 2.

As can be seen from this table with the insoluble polymer almost completely absent initially, the quantity of soluble polymer increased rapidly. Simultaneously with the decrease in the quantity of soluble product after going through a maximum, the percentage of insoluble material increased sharply, and about 4 hours from the start of the polymerization the quantity of soluble product became less than 1% of the original weight of monomer. At this time the conversion of the original monomers to insoluble polymer was practically complete.

Table 1

Results of the Analysis of a Series of Experiments

Expt. No.	Composition of the initial mixture (in millimoles)		Composition of the distillate (in millimoles)		% Conversion, %	Allyl methacrylate content (in molar %)	
	A_o	M_o	A	M		in distillate	in copolymer
1	1.516 (8.1)[1]	17.19	1.210	14.660	15.26	7.62	10.28
2	1.516 (8.1)[1]	17.19	0.885	8.983	47.12	8.97	7.14
3	7.476 (44.25)[1]	9.42	6.254	8.07	15.34	43.66	47.4
4	7.476 (44.25)[1]	9.42	5.794	6.84	24.95	45.86	39.49
5	10.439 (64.93)[1]	5.637	8.350	4.540	19.85	64.80	65.50
6	10.439 (64.93)[1]	5.637	0.217	0.657	95.05	24.83	67.69

Table 2

Results of Investigation of the Kinetics of Formation of Copolymer

Expt. No.	Charge					Duration of expt. (in hrs)	Obtained			
	Methyl methacrylate		Allyl methacrylate		Benzoyl peroxide (in g)		Soluble polymer		Insoluble polymer	
	(g)	(%)	(g)	(%)			(g)	(in % of amount charged in)	(g)	(in % of amount charged in)
Ia	1.719	90	0.191	10	0.0095	1	0.097	5.06	--	0
Ib	1.719	90	0.191	10	0.0095	2	0.046	2.4	0.443	23.2
Ic	1.719	90	0.191	10	0.0095	3	0.012	0.61	1.071	56.1
Id	1.719	90	0.191	10	0.0095	4	0.003	0.16	1.801	94.3
IIa	1.719	90	0.191	10	0.0095	1	0.057	2.90	0.067	3.51
IIb	1.719	90	0.191	10	0.0095	2	0.023	1.20	0.511	26.8
IIc	1.719	90	0.191	10	0.0095	3	0.014	0.73	1.571	82.4
IId	1.719	90	0.191	10	0.0095	4	0.007	0.36	1.855	97.3

[1] The quantity of A_o (molar %) is given in parentheses.

Analogous results were obtained by Simpson [3], for diallyl phthalate and by Rutcvsky and Leznov [4] for different multifunctional monomers.

In Table 3 are given the results of the fractionation of the initial polymerization products.

The dependence of the specific viscosity (η_{sp}) and of the ratio of this quantity to the concentration (C) on the concentration for the same initial copolymer and polymethylmethacrylate is shown in Table 4.

Curves showing the dependence of η_{sp}/C on C give the limiting value of η_{sp}/C for polymethylmethcrylate as $\eta_{sp}/C_{C \to 0} = 1.25$ and for the initial copolymer as $\eta_{sp}/C_{C \to 0} = 0.35$.

Table 3

Results of Fractionation of the Initial Polymerization Product

Methanol added (in ml)	Weight of deposit (in g)	Quantity of precipitate (in % on the polymer content in solution)
24.7	0.035	28.7
25.7	0.066	54.1
26.7	0.087	71.3
27.7	0.099	81.2
29.7	0.115	94.4
34.9	0.122	100

Table 4

Dependence of the Specific Viscosity of the Copolymer and of Polymethyl Methacrylate on the Concentration

Initial copolymer			Polymethyl methacrylate		
Concentration (in %)	η_{sp}	η_{sp}/C	Concentration (in %)	η_{sp}	η_{sp}/C
0.5	0.58	1.15	0.5	0.805	1.61
1	1.425	1.425	1	1.98	1.98
2	4.78	2.39	2	5.67	2.83
4	21.25	5.31	4	19.9	4.97

Thus, although the average molecular weight of the initial polymer was somewhat smaller than that of polymethyl methacrylate, it is a high molecular compound, like the latter.

To find out the conditions of the transition of the soluble polymer to the insoluble one, 10 ml of a 10% solution of the initial product in benzene (starting from 10% allyl methacrylate) was introduced into two ampoules. To the first of these was added 0.5% (on the initial product) of benzoyl peroxide and to the second, in addition to the benzoyl peroxide, 1 ml of methylmethacrylate.

After two days a strongly swollen gel had separated from the liquid in the ampoule containing the methyl methacrylate. On the following day there was no free liquid in the ampoule. In the ampoule not containing monomer, no change was noted. The gel did not dissolve in other organic solvents. The same effect was obtained by adding vinyl acetate and vinylidene chloride, of which the vinyl acetate acted more rapidly than methyl methacrylate (1 day) and vinylidene chloride more rapidly still ($\frac{1}{2}$ day). By diminishing the amount of monomer 5-fold the same sort of precipitation was obtained, although because of the strong dilution its appearance was much retarded. In the complete absence of the monomer the gel did not form even after heating at 65° for two weeks.

Discussion of the Results

The process of copolymerization can be described by the equations [5];

$$dA/dM = A/M \cdot \sigma A + M/\rho M + A = A/M \cdot \frac{\sigma A/M + 1}{\rho + A/M} = A/M \, \underline{f}(A/M) \qquad (1)$$

where σ and ρ are the coefficients of copolymerization, A and M are the molar concentrations of allyl and methyl methacrylates.

Expanding $f(A/M)$ in a Taylor series:

$$f(A/M) = f(A_0/M_0) + f'(A_0/M_0)(A/M - A_0/M_0) + \frac{f''(A_0/M_0)}{2!}(A/M - A_0/M_0) + \cdots$$

we see that all the members of this series, apart from the first, contain the quantity $A/M - A_0/M_0$, where A_0 and M_0 are the initial concentrations of the monomers, and A and M are the same concentrations at any moment of time. As is shown by Tables 1 and 5, in the initial stages of the copolymerization of methyl and allyl methacrylates, $(A_0/M_0) - (A/M)$ is small, not exceeding 6.5%. Hence to a first approximation the expansion can be limited to the members of $f(A_0/M_0)$ of the series shown, and we can write:

$$\frac{dA}{dM} = \frac{A}{M} \cdot \frac{\sigma \cdot \frac{A_0}{M_0} + 1}{\rho + A_0/M_0}$$

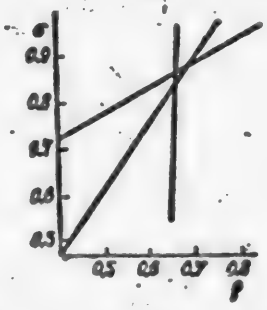


Fig.1. Graphical representation of the equations, obtained by inserting values of A, A_0, M and M_0 from Expts. 1,3, and 5 into Equation (2).

Table 5

Results of the Analysis of a Series of Experiments

Expt. No.	A_0M_0	A/M	$A_0/M_0 - A/M$	$A_0/M_0 - A/M$ (in %)
1	0.0884	0.0826	0.0058	6.56
3	0.793	0.774	0.019	2.4
5	1.853	1.842	0.011	0.59

Integrating within the limits A_0 to A and of M_0 to M and rearranging, we obtain the equation:

$$\rho \cdot \frac{\ln M/M_0}{\ln A/A_0} - \sigma \cdot \frac{A_0}{M_0} = 1 - \frac{A_0}{M_0} \cdot \frac{\ln M/M_0}{\ln A/A_0} \quad (2)$$

In the integration, the values of A, A_0, M and M_0 were taken as constants since they do not change during the time of reaction.

Inserting the values of A, A_0, M and M_0 for experiments 1,3,5 we obtain the equations of three straight lines.

$0.0623 \cdot \sigma - \rho = -0.6177$; $0.6194 \cdot \sigma - \rho = -0.077$; $1.785 \cdot \sigma - \rho = +0.894$

A plot of these in the form of curves of σ against ρ, (Fig.1) shows that the straight lines, when intersecting, form a small triangle. The values of σ and ρ sought for lie within the triangle and are $\sigma = 0.87 \pm 0.025$ and $\rho = 0.69 \pm 0.02$.

In further calculations the average values of $\sigma = 0.87$ and $\rho = 0.69$ were used.

The fact that σ and ρ are also less than unity shows that the monomer units entering into the composition of the copolymer, have a definite tendency to alternate. In actual fact, since $\sigma = K_1/K_2$ is less than 1, K_1 is less than K_2, and the radical R_A reacts more "willingly" with methyl methacrylate than with allyl methacrylate, and the same is true for the radical R_M. The tendency of the monomeric units to alternate, however, does not mean that such an alternation

will always occur, because the probability of this meeting of a radical with one or other of the monomers depends not only on the rate constants, but also on the concentration of the monomers in the reaction mixture.

Between A, M, σ, ρ and the allyl ester content in the copolymer (A') there exists the relationship [5]:

$$A' = \frac{\sigma A^2 + AM}{\sigma A^2 + 2AM + \rho M^2} \qquad (3)$$

Strictly speaking, these formulas apply only to the first moments of reaction, since A is the differential composition of the polymer for each moment of time.[1] But Table 1 shows for the initial stages of polymerization, when the degree of polymerization did not exceed 20%, that the composition of the monomer mixture changed by less than 1% and for the later stages (excluding Expt.No.6) by less than 2%. Hence the use of Formula 6 for calculation is quite justifiable.

As can be seen from Fig.2, containing a graphical representation of Equation 3 from experimental values of A and A', the experimental points lie exactly on the curve only for the initial stages of the polymerization, when the polymerization becomes more extensive, accompanied by the formation of insoluble products and the destruction of the homogeneity of the system, there are considerable deviations.

Furthermore, investigation of the kinetics of the formation of the soluble and the insoluble polymers suggests that the copolymerization of allyl and methyl methacrylates proceeds in two steps: a) with the formation of a soluble polymer; and b) the transition of the soluble polymer to an insoluble one.

Thus, the indicated deviations of the experimental points from the theoretical curve cannot be explained only by the appearance of a new phase, or by the destruction of the conditions under which the Equation for the differential composition can be applied. (In Expts. 2 and 4, (Table 1), in spite of the presence of a fairly considerable amount of insoluble gel, the allyl methacrylate content in the distillate differs little from that in the original mixture of monomers). They can be explained also by the fact that, on the primary process of the formation of soluble copolymer, is superimposed the secondary one of the transition of the soluble to the insoluble form.

The smooth character of curves of the fractionation of the initial soluble confirms that this product actually is a copolymer of allyl and methyl methacrylates, and not a mixture of polymethyl- and polyallylmethacrylates. In the case of the formation of a mixture of two polymers, curves with two bends in them would be obtained, corresponding to the initial precipitation of each polymer [5].

Furthermore, comparison of the curves showing the dependence of η_{sp} on C and of η_{sp}/C on C, for the initial copolymer and polymethyl methacrylate shows that the molecules of these substances are near to one another both in form [7]

---

1) By integrating Equation 1, Gindin obtained a formula for the calculation of the integral composition of the copolymer. The calculation was made graphically, in view of the complexity of the function obtained. It is extremely characteristic that for the systems he investigated (butadiene and acrylonitrile), the differential composition of the copolymer differed little from the integral one even when the degree of polymerization reached 50%.

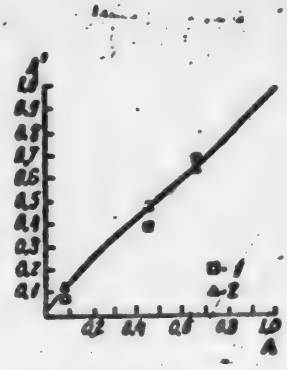


Fig.2. Graphical representation of Equation 3 from experimental values of A and A'. 1 – initial stage; 2 – later stage.

and size, i.e., the molecules of the initial polymers are basically linear. The fact that the initial polymer is soluble is a confirmation of this, for this would be impossible for so large a molecular weight and for an already "latticed" molecule. This means that in the initial stages of the polymerization only one double bond from the molecule of allyl methacrylate participates, and the second one does not react.

Gindin [8] showed that in the polymerization of allyl methacrylate in solution, a soluble polymer is formed, and that the allyl group practically does not participate in the polymerization. An analogous result was obtained in the investigation of the product of the photo polymerization of allyl methacrylate [9].

On the other hand, as Berlin and Bogdanov found [10], with two active methacrylate groups in the monomer, a soluble polymer is not obtained at all.

Thus, in the formation of the initial copolymer, in all probability, the double bonds of one methacrylic group participated. Only the presence of the less active allyl group in the side chains of the polymer molecules can explain the formation of the soluble copolymer in general and the fact that it does not convert to the insoluble form even after two weeks heating at 65°.

The fact that it is impossible for the "laced" molecules of the soluble polymer to form cross-linked molecules easily in the presence of even small quantities of the monomer, containing active vinyl groups, not only confirms that in the transition of the initial polymer to the insoluble state the monomer participates, but also shows that this transition is a process of secondary copolymerization between the monomer and the initial copolymer.

In the process an essential role is doubtless played by purely steric factors, as a result of which the more mobile (compared with the polymer) molecules of the monomer can approach the allyl groups of the macromolecule far more easily than the allyl groups of the adjacent polymer molecule.

With a large amount of allyl methacrylate in the initial copolymer, the "concentration" of allyl groups of the side chains is larger, as a result of which the chance of a successful collision between linear macromolecules (both between themselves, and with monomer molecules) increases very much. This also explains why it is so difficult to separate the initial soluble product at higher concentrations of allyl methacrylate in the initial mixture of monomers.

In the process of secondary copolymerization and building up of insoluble polymer, the distribution of the polymer units A and M on the linear macromolecules, has a considerable effect since the linking of the latter can only occur where there are side groups with free double bonds, i.e. at those places where there are allyl methacrylate residues.

The average distance between two possible positions of linking depends on the quantity of M residues between two A ($\bar{l}_M$) and the quantity of A residues between two M($\bar{l}_A$). As can easily be shown [7]

$$\bar{l}_M = \frac{\sigma M + A}{A} = \frac{\sigma(1-A) + A}{A}; \quad \bar{l}_A = \frac{\sigma A + M}{M} = \frac{\sigma A + (1-A)}{(1-A)}$$

The results of the calculation of L_M and L_A as functions of A are shown in Fig.3 from which it can be seen that at small values of A the number of A residues in the units of the chain tends towards unity, and the distance between the allyl groups is large. As a result of this the likelihood of lacing in the polymerization of mixtures with small amounts of A is small, and the product obtained should contain a certain quantity of linear macromolecules. With large initial content of A the probability of lacing is much greater, but, since A enters into reaction faster than M (since the concentration of A is larger), the quantity of A in the monomer mixture will be lowered, which in turn will diminish the likelihood of lacing. This apparently explains why such copolymers reveal certain properties characteristic of linear polymers, in spite of the fact that they consist basically of latticed [11] molecules.

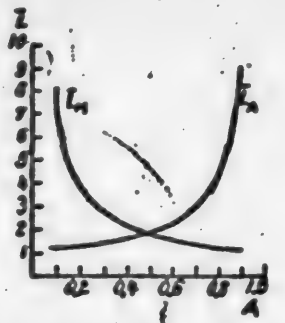


Fig.3. Graphical representation of the calculation of the change of L_M and L_A as a function of A.

SUMMARY

1. The copolymerization of allyl methacrylate proceeds through the stage of formation of soluble copolymers, which are converted to insoluble ones by interaction with the monomer.

2. The transition to the infusible state appears to be a process of copolymerization of the initial soluble copolymer with the monomer. The rate of this process depends on the concentrations and the chemical natures of the monomers.

3. The formation of the initial soluble product is a normal process of copolymerization leading to the formation of predominantly linear macromolecules.

In the calculation of the constants of copolymerization by an approximate formula we obtain the values:

$$\sigma = 0.87 \pm 0.025 \text{ and } \rho = 0.69 \pm 0.02$$

4. The deviation of the copolymerization from this theory in the later stages of the process is explained by the superposition of secondary copolymerization of the linear macromolecules with the monomers, on the initial process.

LITERATURE CITED

[1] Rutovsky and Shur, J. Appl. Chem. 24, 8 (1951).[1)]

[2] Rutovsky and Shur, J. Appl. Chem. 24,10 (1951).[2)]

[3] L. Simpson, J. Chem. Soc. Ind., 65, 4, 106 (1946).

[4] Rutovsky and Leznov, J. Appl. Chem. 22, 887 (1949).

[5] Rutovsky and Leznov, High Molecular Compounds, 6, 1 (1947).

[6] Gindin, Abkin and Medvedev, J. Phys. Chem. 21, 11, 1269 (1947).

[7] H. Mark, Phys. Chem. High. Polymer Syst., 284 (1940).

[8] Gindin, J.Gen.Chem. 19, 9, 1694 (1949).[3)]

[9] H. Blout, E. Ostberg, C.A., 40, 4912 (1946).

[10] Berlin and Bogdanov, J.Gen.Chem. 17, 9, 1699 (1947).

[11] Rutovsky and Shur, J.Chem.Ind., 7/8, 6, 1946.

1) See Consultants Bureau English Translation, p. 967.
2) See Consultants Bureau English Translation, p. 1221.
3) See Consultants Bureau English Translation, p. a-127.

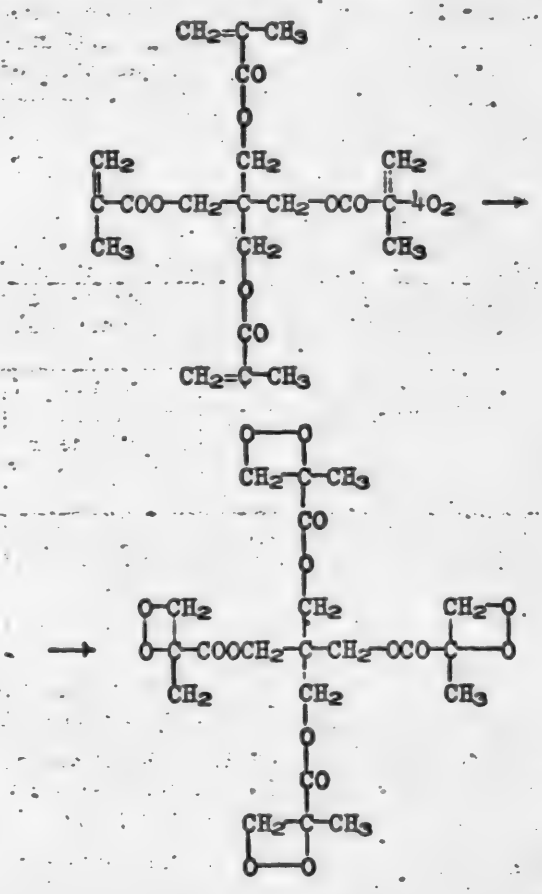
Received September 11, 1950.

TRANSFORMATION OF POLYMERS IN THE PRESENCE OF THE PENTAERYTHRITOL ESTER OF METHACRYLIC ACID [1]

A. Ya. Drinberg, Sh. N. Golant, and L. I. Goldfarb

Lensoviet Technological Institute, Leningrad

In a previous communication [1] it was shown that in the presence of the penterythritol ester of methacrylic acid, linear saturated esters are converted to spatial polymers. It must be noted that the ester mentioned very rapidly forms peroxides in air [2], and it is thus the peroxide of pentaerythritol methacrylate which acts on the linear polymer. Since the ester has four saturated bonds, 1-4 peroxidic groups can be formed:



[1] Communication II dealing with the conversion of linear saturated to spatial polymers.

Apparently these groups cause the polymer chains to link together, in the same way as does benzoyl peroxide.

$$\begin{matrix} C_6H_5CO-O \\ | \\ C_6H_5CO-O \end{matrix}$$

Since it is known that metallic salts, particularly cobalt ones, accelerate peroxide formation, it could be expected that the presence of cobalt soaps would accelerate the formation of the peroxide and hence of the polymer.

EXPERIMENTAL

A 50% solution of cobalt resinate was used, of which enough was added to give 0.129% of Co on the weight of pentaerythritol methacrylate.

The solutions of polymer were spread on previously weighed glass plates, which were placed in a thermostat at 100°. After 4 hours drying at this temperature the plates were weighed, placed in a filter paper thimble in a Soxhlet apparatus for extraction. The weight of the dried films was 0.3-0.5 g. The extraction was made with the same solvent in which the initial polymer was dissolved [1]. After extraction for 6 hours the plates were removed, dried, and weighed so as to determine the quantity of residual insoluble polymer in them. For each type of polymer the degree of conversion was checked by the performance of 6 experiments in parallel.

The average data are presented in Table 1.

TABLE 1

Comparative Data on the Transformation of Saturated Linear Polymers of Pentaerythritol Methacrylate (PM) at 100° for 4 hours

Linear polymer	Composition of the films (in %)		Trimeric polymer obtained (in %)		
	PM	Linear Polymer	Total quantity	Amount obtained from linear polymer	Quantity of linear polymer converted (in % of the original linear polymer)
Polybutylmethacrylate	23	77	70.0	47	61.0
Pervinylchloride. . .	23	77	85.7	62.7	81.5
Polythene.	23	77	91.3	68	88.0
Polyvinylchloride. .	23	77	99.0	76	99.0

Films not containing PM, treated under identical conditions, dissolved completely on extraction. Films dried at 20° likewise dissolved completely.

In order to elucidate the effect of the PM concentration on the transformation of the linear polymer, the quantity of the latter was diminished 2-fold. Thus, the concentrations of the components were:

Linear polymer 89.5%, PM 11.5%. The conversion data are set out in Table 2.

Comparison of Tables 1 and 2 shows that as the concentration of PM in the films diminishes, the quantity of linear polymer converted to the trimeric variety decreases.

The effect of concentration of PM on the transformation of mixtures of it with polybutylmethacrylate to the trimeric form in the presence of a

cobalt soap is shown in Table 3.

From the data tabulated it can be concluded that, simultaneously with the conversion of the tetramethacrylic ester of pentaerythritol there occurs the conversion of the linear polymer to the irreversible state. However the quantity of polybutylmethacrylate, converted to trimer, increases with increase of the concentration of the "linking agent" only up to a definite limit (50%) after which it falls off somewhat.

TABLE 2

Comparative Data on the Transformation of Polymers

Polymers	Quantity of Trimer (in %)		
	Total quantity	Amount formed from linear polymer	Quantity of linear polymer converted, as a ratio of the original linear polymer
Pervinylchloride	35.6	24.1	26.9
Polythene. . . .	40.0	29.5	33.0
Polyvinylchloride	42.2	30.7	34.5

An idea of the kinetics of the process can be got from the data set out in Table 4 (PM concentration 2%).

Table 3

Effect of the Concentration of PM on the Transformation of its Mixtures

PM (in g per 100 g of polybutylmethacrylate)	0	10	20	30	40	50	60	70	80	90
Tetramethacrylic ester content (in %)	0	9.1	16.6	23.2	28.6	33.3	37.5	41.2	44	47.4
Total quantity of insoluble polymer (in %)	0	26.97	48.3	68.3	70.3	74	66	69	74.2	74
Linear polymer converted (in %)	0	19.7	38	57.5	58.4	60.0	45.2	47.3	54.0	50.0

From Table 4 it can be seen that the transformation reaches 69% after 7 hours at 100°. In the absence of the cobalt soap catalyst, there is no transformation.

Study of the properties of the transformed and untransformed films, based on poly- and pervinylchlorides at 100° revealed that the inelastic moduli and impact strength were low.

In order to find out the optimum conversion temperature, the experiments were repeated at intervals in the range 40-100°. The effect of temperature on the linking process is shown in the Figure. The linking process for poly- and pervinylchlorides is quite fast above 60°. Raising the temperature lowers the physicomechanical properties of the films already referred to.

Table 4

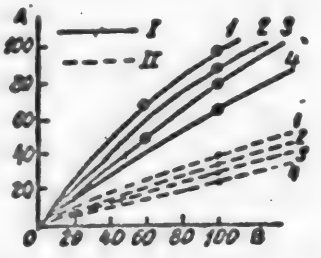
Kinetics of the Transformation of Linear Polymer to the Irreversible State

Duration of transformation (in hours)	1	1.5	2	3	4	5	6	7	8	9	10	20
Quantity of trimeric polymer (in %)	8.6	19	30.7	36.5	57.5	59.3	67.9	69	69	69	70.5	70.5
Quantity of linear polymer transformed to the insoluble state (in % on the original)	0	0	10	17.3	44.8	47	58.3	59.5	59.5	59.6	61.8	61.8

Table 5

Transformation of Poly- and Pervinylchloride Films at 60° and 100°.

Polymers	Quantity of polymer transformed (in %)			
	100°		60°	
	Total quantity of trimer produced from linear polymer	Quantity of linear polymer transformed, as a percentage of the original polymer	Total quantity of trimer produced from linear polymer	Quantity of linear polymer transformed, as a percentage of the original polymer
Polyvinylchloride	76	99	51	69
Pervinylchloride	62.7	81.5	33	43



Effect of temperature on the linking in the presence of PM. A) percentage of transformation of linear polymer; B) temperature (in °C). I) 2% PM; II) 11.5% PM. 1) polyvinylchloride; 2) polythene; 3) pervinylchloride; 4) polybutylmethacrylate.

In Table 5 are given comparative data about the transformation of the polymers at 60 and 100°. The concentration of PM was 30% on the weight of the polymer (23% in the film).

The adhesion of films was tested both on pure films and those containing PM. It was determined by the Snedz adhesometer. Comparative data are given in Table 6. (averages of 6 experiments.)

From this table it can be seen that, as the quantity of polymer transformed increases the adhesion of the films increases as well.

PM can transform to the trimeric polymer at ordinary and at elevated temperatures in the presence of cobalt soaps. At normal temperatures the transformation is slow, while at higher temperatures complete transformation is attained in the course of one hour. The quantity of trimer was determined [1] from the quantity of insoluble residue, after extracting the films in benzene for 6 hours. The results of the investigation are set forth in Table 7.

Table 6

Effect of Transformation of Polymer on the Adhesion of the Films.

Linear polymer	Pervinylchloride at 60°		Polybutylmethacrylate at 100°		Polyvinylchloride at 60°	
	pure	with PM	pure	with PM	pure	with PM
Total quantity of trimer (in %)	0	55	0	70	0	74
Adhesion (in g/mm)	300	490	296	630	300	790

Table 7

Transformation of PM to Trimer

Transformation temperature (in °)	Time (in days)	1	2	3	30	60	180
20	Trimer (%)	-	-	10	14	18	28
	M.p. (in °)	64	-	65	-	75	200
100	Time (in minutes)	15	45	60	75	90	120
	Trimer (%)	-	78	82	89	100	100
	M.p. (in °)	64	-	300	infusible		

To assess the extent of transformation of the PM itself, in binary mixtures with polybutylmethacrylate, it is of the first importance to elucidate the degree of utilization of the unsaturated groups of PM. Attempts to determine the residual unsaturation of the films after transformation were made by bromination with bromine vapor in the dark. This was done with pure PM, and then with a binary mixture of the latter with polybutylmethacrylate. With increase in the quantity of unsaturated compound transformed, and with decrease in the percentage of the soluble fraction, the bromine number should decrease.

A 50% solution of PM in xylene, in the presence of cobalt resinate (0.129% Co) was spread on a glass plate, which was kept in a thermostat at 100°. After a definite interval of time the plates with the adherent films were taken out of the thermostat, cooled down and then extracted with benzene. In parallel with other tests, the bromine number of these films was determined by bromination with bromine vapor in the dark. It was established that HBr was not formed, i.e. that there was no metalepsis. With increase in the time of transformation the quantity of soluble product diminished; after 1½ hours the PM was 100% transformed to trimer.

Table 8

Comparative Data on the Transformation of Pure PM at 100° by Extraction and Bromination

Duration of the transformation (in minutes)	Bromine Number [1]	Quantity of trimer calculated from the bromine number	Quantity of trimer by extraction
0	146.0	0	0
30	139.5	4.5	4.5
45	52.0	51.7	52
60	50.0	68.5	70
75	9.4	92	90
90	0.0	100	100

In Table 8 are set out the average results (of 4 determinations) on the transformation of pure PM at 100° (by extraction and bromination).

These data show that it is possible to use bromination for the approximate control of the process.

The comparative determinations of the bromine number of PM by the standard bromate method showed that the bromine vapor method gives values closer to the theoretical (average of 4 determinations).

Theoretically calculated bromine number	Bromine number from bromate method	Bromine number from Br vapor method
156.5	132	146

Apart from this, the bromine vapor method is to be preferred for its simplicity. When determining their Br Nos. by the bromate method the samples of PM polymerized, which explains the lower values thus obtained.

For finding out the character of the transformation at 20° the peroxide numbers of films were determined by the following method. A weighed quantity of ester (2-3g) was dissolved in 30-45 ml of a mixture, in different proportions of chloroform and anhydrous acetic acid. 1 ml of a solution of KI, saturated in the cold, was added, and after 15-20 seconds the iodine liberated was titrated in the cold with 0.01 N $Na_2S_2O_3$. The peroxide number was calculated from the formula

$$P.n. = \frac{(a-b)\cdot 0.001269\cdot 100}{W} = \frac{(a-b)\cdot 0.1269}{W},$$

where a is the quantity, in ml, of 0.01 $Na_2S_2O_3$ used up in titrating the iodine, b the number of ml of thiosulfate used in the blank experiment, and W is the weight of ester taken for analysis.

[1] Theoretical bromine number for the monomer 156.6.

We give here the p.n.'s for the results of the polymerization of PM at 20°.

Duration of experiment (in days) at 20°	24	72	120	720	4500
P.n. (in % I_2)	0.3	0.48	0.94	1.32	1.57

The increase of the P.n. demonstrates that the transformation of the ester to the trimer goes through the peroxide by a process of autoxidation, as happens with drying oils. It is known that peroxides decompose at high temperatures; hence peroxide cannot be found at temperatures of 100°, i.e. at the linking temperature. The possibility of transforming both pure PM and a mixture of PM and polybutylmethacrylate at 60° was investigated. The p.n.'s of the films were determined. The data are given in Tables 9 and 10.

Table 9
Conversion of PM at 60°

Duration of conversion (in minutes)	15	30	45	60	75	90
Quantity of trimer (in %)	11	20	98	100	100	100
P.n. (in % I_2)	1.55	1.42	0.95	0.41	0.3	0

Table 10
Transformation of Mixture of 77% Polybutylmethacrylate and 23% PM at 60°

Duration of conversion (in hours)	1	2	3	4	5	6
Quantity of trimer (in %)	0	51	54	58	66.8	67.1
Quantity of trimer produced from linear polymer (in %)	0	28	31	35	43.8	44.1
Quantity of linear polymer transformed expressed as a percentage of the initial linear polymer	0	55	57.5	60	65.5	70.8
P.n. (in % I_2)	3.3	2.3	1.5	1.1	1.1	1.1

Linking does not occur in the system of saturated polymer polybutylmethacrylate in a non-oxygenated solvent in the absence of a catalyst, and when a catalyst is present the reaction only occurs with PM: there is no transformation of polybutylmethacrylate in the presence of 3% benzoyl peroxide at 170-180° in a stream of carbon dioxide. In air, 75-77% of linear polymer is transformed.

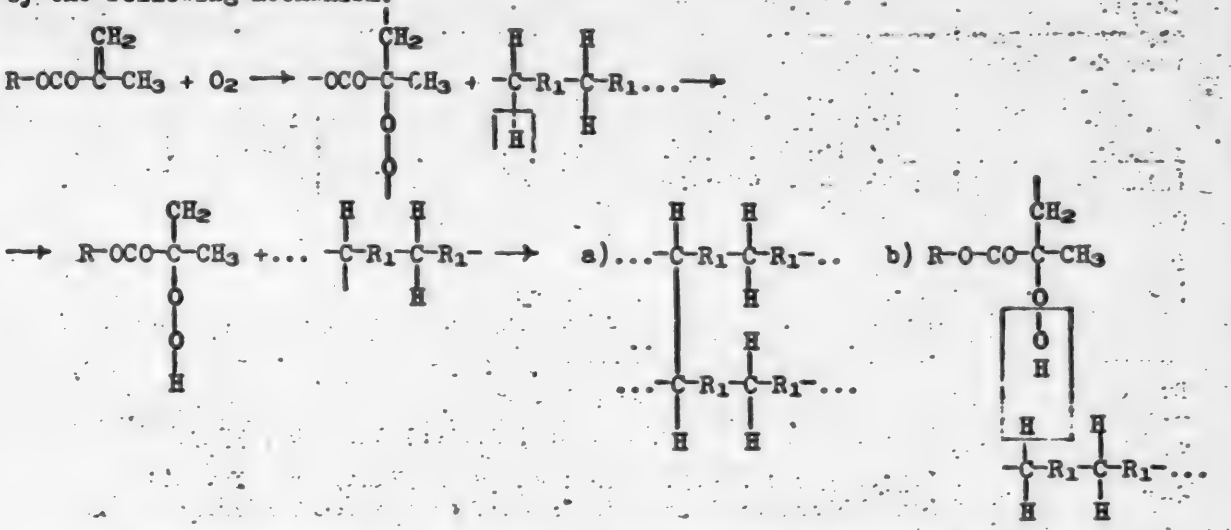
It can be suggested on the basis of this investigation that the process of linking of the saturated linear polymer via PM and in the presence of a catalyst is a chemical one.

The free peroxide radical of PM, formed in the presence of oxygen and of active oxygen "carried" by the cobalt soap, initiates the activation of the linear polymer macromolecule. PM itself (unsaturated polymer) can condense as a result of thermopolymerization in a stream of carbon dioxide, and as a result of polymerization in air in the presence of a catalyst.

It it is supposed that the loss of solubility of the linear polymer occurs at the expense of the building of the saturated polymer into the trimeric form of pentaerythritol methacrylate, then the linking should occur in such a system in a stream of carbon dioxide. However, the linear polymer does not transform in carbon dioxide, while under the same conditions PM goes completely to trimer. In the presence of atmospheric oxygen, the transformations of linear polymer and of

PM proceed simultaneously. Thus, the absence of oxygen, which forms active peroxide radicals, apparently prevents the linking of the saturated polybutylmethacrylate. There is also no transformation in the absence of a catalyst (oxygen carrier), namely cobalt soap.

The chemical character of the linking process is also supported by the transformation of linear polymers in the presence of benzoyl peroxide. In this case, the transformation occurs only in the presence of atmospheric oxygen. It may be suggested that the linking in the presence of PM can occur by the following mechanism:



As can be seen from Table 10, at 60° transformation always goes through the peroxide.

To confirm the chemical character of the linking of the linear polymer via peroxide, the transformation of films of PM and of its mixture with polybutylmethacrylate was studied at 100° in air, and in anaerobic conditions (stream of carbon dioxide) in the presence of cobalt resinate as a catalyst.

The glass plates, with the film-forming solutions on them, were placed in a flask from which the air had previously been displaced with a stream of purified carbon dioxide. The flask with the plates was placed in a thermostat at 100°. Carbon dioxide was passed continually through the flask. In parallel with this, plates exposed directly to the air and covered with the same film-forming solution, were placed in the thermostat. After exposure for 6 hours the films were extracted with benzene.

The data are set out in Table 11.

Experiments showed that the linking of PM alone, i.e. the unsaturated monomer, proceeds both in an oxygen-containing atmosphere and also in one not containing oxygen, both in the presence of a catalyst and in its absence.

SUMMARY

1. By bromination in the dark it was shown that the fall of bromine number is parallel with an increase in the quantity of trimer.

2. It has been shown that the transformation to trimer goes through a peroxide stage.

Table 11

Transformation of PM and of its Mixture with Polybutylmethacrylate in Air and in a Stream of Carbon Dioxide at 100°

Temperature (in °C)	Polymers	Quantity of trimer (in %)	
		Transformation in air	Transformation in carbon dioxide
100	PM with catalyst	100	100
100	23% PM, 77% polybutylmethacrylate	70-72	19-21
100	PM without catalyst	100	100
100	23% PM, 77% polybutylmethacrylate without catalyst	0	0
175	23% PM, 77% polybutylmethacrylate, 3% benzoyl peroxide	75-77	0

3. It has been shown that the transformation only goes in an oxygen-containing atmosphere in the presence of an oxygen carrier, a cobalt soap. In CO_2 the process does not occur.

LITERATURE CITED

[1] A. Ya. Drinberg, and Sh. N. Golant., J. Appl Chem. 10 (1951).[1)]

[2] A. Ya. Drinberg and Sh. N. Golant and B. M. Fundyler. Investigations in the Field of High Molecular Compounds (Report to the 6th Conference, USSR Acad. Sci.), 172 (1949).

Received November 27, 1950.

[1)] See Consultants Bureau English translation, p. 1225.

INTERACTION OF GELATIN WITH VEGETABLE TANNING AGENTS[1)]

A. Pasynsky and A. Popova

A. Bach Institute of Biochemistry of the USSR Academy of Sciences

In the tanning of collagen, processes connected with the kinetics of tanning have a considerable influence on the direct interaction of collagen with tannins. As a result of the complicated morphological structure which is characteristic of collagen, the results of tanning depend very much on the conditions of diffusion of solutions of the tanning agent, on its degree of dispersion, on the conditions of preparing the hide for tanning, etc. In the study of the processes of direct interaction of collagen and tanning agent under equilibrium conditions, it is desirable to eliminate factors which slow down the kinetics of the tanning.

This may be achieved by using gelatin in the form of gels or solutions instead of collagen; gelatin, in its amino acid content and chemical properties, is sufficiently close to collagen [1]. It is necessary to mix the solutions of tanner and gelatin directly, since spreading the solution of tanner on gelatin gel, a method which is used in many investigations, completely preserves the kinetic factors mentioned above.

It is thus necessary to select a corresponding method of control of the tanning process. Usually, in all investigations and in practical analyses, the quantity of tanner bound with the gelatin or collagen is determined by the weight of the tanned sample, after carefully washing it free from excess tanner with water, buffer solution, or alcohol. In this, the original equilibrium of the albumen relative to tanner is naturally displaced, and the determination of the quantity of bound tanner corresponds to nonequilibrium conditions.

In planning our study of the process of tanning under equilibrium conditions, we made use of the fact that, in the tanning of collagen or gelatin, some of the ionogenic groups of the albumen and tanner are blocked, as a result of which the acid and alkali equilibrium in solutions is changed. For this purpose we made a comparison of potentiometric titration curves for gelatin and the tanners investigated, taken separately, with the curves of titration of mixtures of both solutions. The deviation of the curves for the titration of mixtures of gelatin and tanner, from those which would be obtained by simple addition of the titers for the separate components of the mixture, can serve as a direct measure of the interaction of gelatin and tanner in the given region of pH. Thus, this interaction was measured by us as the degree of blockage of the ionogenic groups of gelatin and tanner (as a result of the direct interaction of these groups or by some other mechanism), reflected on the course of the potentiometric titration curve. The establishment of equilibrium was immediately shown by the constancy of the pH measured. This method of measurement, in addition, made it possible to eliminate variations in the properties of the individual samples taken for investigation, because in comparing the curves these deviations were automatically excluded.

Thus, the object of our work was the comparative potentiometric study of the interaction of gelatin and tanner under equilibrium conditions.

---

1) Communication 1 of a series dealing with the potentiometric study of the interaction of gelatin with tanners.

EXPERIMENTAL

Samples of photographic gelatin were purified by Loeb's method, with subsequent dialysis to an ash content of 0.02%, and dried in vacuum at room temperature; the solutions were prepared from weighed quantities of the dried preparation. A 2% solution of gelatin had a pH of 5.05, and an electrical conductivity of $1.8 \cdot 10^{-5}\ \Omega^{-1}$.

As vegetable tanners, pure tannin (Kahlbaum) and oak extract were used; some of the experiments were carried out with quebracho. After preparation, the solutions were allowed to stand and were then filtered.

The potentiometric measurements were carried out with a glass electrode; those in the region of pH 8-12 were made in an atmosphere of nitrogen. For this purpose, the end of a microburette and two tubes for leading in and out the stream of nitrogen, were hermetically sealed through the paraffin wax cover of the vessel containing the glass electrode. The nitrogen was obtained from a gasometer and was passed through a train of pyrogallol wash bottles. Titration was made with 0.1 and 1.0 N solutions of HCl and NaOH (at pH 8-12 KOH was used) on pure aqueous solutions of gelatin and tanner (we avoided complication of the equilibrium by the addition of neutral salts or of weak acids and bases). All the titrating solutions were prepared in identical volumes, for example: 20 ml 0.5% gelatin solution, 20 ml 1% tanning agent solution and a mixture of 10 ml 1% solution of gelatin and 10 ml of 2% tanning agent solution (the latter mixture was kept at room temperature for 1-2 hours before titration). After addition of successive portions of the acid or alkali solutions during titration, the solutions were maintained for 15-20 minutes to check the constancy of the pH. All titrations were repeated in duplicate on different samples, with good reproducibility.

The bound H^+ ion concentration (C_H^b) was determined from the formula:

$$C_H^b = C_1 - \frac{a_H}{f_a}$$

where C_1 is the analytic (total) concentration of H^+ ions in solution, a_H is the activity of H^+ ions measured potentiometrically, f_a is the activity coefficient of the H^+ ions in solution which f equals f_a for the pure acid at the same activity of the H^+ ions. In an analogous manner, the quantity of bound OH-ions when titrating with alkali was calculated.

The results of titrations for systems with tannins and oak extracts are set out in Tables 1 and 2. In each table three curves of titration for the systems gelatin/tanner and for separate components of the systems are compared. Only the equilibrium values of pH and the quantities of bound H^+ or OH ions are given (the data for the latter are denoted in the table by a minus sign), the other quantities (e.g. C_1) can easily be calculated from them.

In the last column of each table are given the values of the algebraic differences between the curves of titration of the mixture and the sum of the titration curves for the components of the mixture. These differences, as already indicated, characterize the interaction of gelatin and tanning agents in the pH range studied.

Discussion of the Results

As has been indicated, the quantity of bound tanner is usually determined as the quantity of most firmly bound tanner, which cannot be washed out even on long-continued extraction with solvent [2]. Substances which can be washed out

Table 1

Potentiometric titration of the gelatin-tannin system

pH	Bound $C_H \cdot 10^4$			$\Delta J \cdot 10^4$
	gelatin, 0.5 g	tannin, 1 g	mixture: 0.5 g gelatin + 1 g tannin	
2.0	3.50	–	–	–
2.2	3.40	–	1.83	1.57
2.6	3.20	–	1.46	1.74
3.0	2.75	–	0.87	1.88
3.2	2.35	–	0.55	1.80
3.6	1.70	–	0.0	1.70
4.0	1.10	-0.10	-0.30	1.30
4.2	0.85	-0.22	-0.42	1.05
4.6	0.40	-1.00	-0.80	0.20
5.0	0.0	-2.04	-1.82	0.22
5.2	-0.10	-2.34	-2.20	0.24
5.6	-0.35	-2.78	-2.60	0.53
6.0	-0.45	-3.12	-2.90	0.67
6.2	-0.50	-3.26	-3.00	0.76
6.6	-0.60	-3.40	-3.24	0.76
7.0	-0.70	-3.56	-3.48	0.78
7.2	-0.75	-3.64	-3.58	0.81
7.6	-0.80	-3.80	-3.74	0.86
8.0	-0.90	-3.94	-3.84	1.00
8.2	-0.95	-4.02	-3.90	1.07
8.6	-1.05	-4.20	-4.02	1.23
9.0	-1.15	-4.56	-4.14	1.57
9.2	-1.25	-5.14	-4.20	2.19
9.6	-1.40	-5.40	-4.40	2.40
10.0	-1.65	-5.58	-4.70	2.53
10.2	-1.75	-5.62	-4.90	2.47
10.6	-2.10	-5.64	-5.36	2.38
11.0	-2.40	-5.66	-5.40	2.66

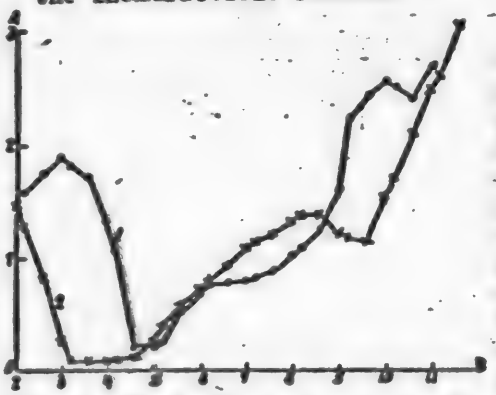
Table 2

Potentiometric titration of gelatin-oak extract

pH	Bound $C_H \cdot 10^4$			$\Delta J \cdot 10^4$
	gelatin, 0.5 g	tanning extract, 1 g	mixture 0.5 g gelatin + 1 g oak extract	
2.0	3.50	1.96	4.00	1.46
2.2	3.40	1.84	3.98	1.26
2.6	3.20	1.50	3.88	0.82
3.0	2.75	1.05	3.52	0.28
3.2	2.35	0.92	3.24	0.10
3.6	1.70	0.56	2.16	0.10
4.0	1.10	0.0	1.02	0.08
4.2	0.85	-0.08	0.87	0.10
4.6	0.40	-0.80	-0.28	0.12
5.0	0.0	-1.39	-1.13	0.26
5.2	-0.10	-1.60	-1.32	0.38
5.6	-0.35	-1.96	-1.75	0.56
6.0	-0.45	-2.32	-2.07	0.70
6.2	-0.50	-2.52	-2.23	0.77
6.6	-0.60	-2.92	-2.62	0.90
7.0	-0.70	-3.24	-2.88	1.06
7.2	-0.75	-3.32	-2.96	1.11
7.6	-0.80	-3.50	-3.12	1.18
8.0	-0.90	-3.64	-3.24	1.30
8.2	-0.95	-3.70	-3.30	1.35
8.6	-1.05	-3.86	-3.56	1.35
9.0	-1.15	-4.04	-4.00	1.19
9.2	-1.25	-4.12	-4.20	1.17
9.6	-1.40	-4.28	-4.56	1.12
10.0	-1.65	-4.74	-4.88	1.51
10.2	-1.75	-4.92	-5.00	1.67
10.6	-2.10	-5.08	-5.12	2.06
11.0	-2.40	-5.20	-5.12	2.48
11.2	-2.60	-5.24	-5.15	2.69
11.6	-2.85	-5.32	-5.17	3.00
12.0	-3.15	–	–	–

with water, depending on their ease of extraction, sometimes divide into free and bound portions [3]. Apart from the insufficiently clear physical meaning of these quantities, it should also be noted that the method of determining them involves the slow kinetics of extraction and usually gives non-equilibrium values. The comparison of the curves for the potentiometric titration of gelatin, tanner and mixtures of the two, which we made in our work gives a different criterion for determining the quantity of bound tanner, this being measured by the displacement of the acid/alkali equilibrium in the system as a result of blocking the ionogenic groups of gelatin and tanner in tanning. This blocking of the ionogenic groups occurs either at the expense of direct interaction between these groups, or as a result of the spatial limitations of the accessibility of these groups

(reactivity), when the tanner is molecularly absorbed on albumen. In the determination, by the potentiometric method, of the quantity of bound tanner, some part of the water-extractible products should be measured, as well as the inextractible residue.



Dependence of the deviation of the titration curve for mixtures of gelatin and tanner on the addivity of pH. A $-\Delta J \cdot 10^4$; B – pH. 1 – Gelatin/tannin; 2 – Gelatin/oak extract.

The relation between the two methods of determining the quantity of bound tanner is analogous to the relation between the methods of precipitation and potentiometric measurement for determining the absorption of acid or alkali by albumens. For example, in the old papers of Spiro and Pemsel [4], Cohnheim and Kruger [5] and others, the bound acid and alkali in albumens was determined after their precipitation by ammonium sulfate or phosphotungstic acid. These determinations had the same defects (disturbance of the initial equilibrium etc.) as in the method of non-extractable residues in the determination of bound tanner, and have consequently been replaced by the methods of equilibrium electrometric measurements. It is necessary, however, to bear in mind that the unextracted residues method gives practically the best characteristic of the connection between the tanner and the physico-mechanical properties of hide.

The data given in Tables 1 and 2 and in the figure show that the magnitude ΔJ (deviation of the titration curves for the mixture from addivity), being a measure of the interaction of the tanner and albumen, exhibits a characteristic change with change of pH. These values differ from zero at all pH's (this reflects the effect of nonionogenic interaction: molecular adsorption of tanner on albumen, reaction with peptide groups of the albumen, etc.) but in the region of the isoelectric point (at pH 4-5) they pass through a definite, clear minimum. In the acid region, ΔJ increases as the acidity increases while in the alkaline region a relative maximum is obtained at pH around 8.5-9.5 (for the tanners investigated) and afterwards, when the solution becomes more alkaline, the curve slopes upward again. The shape of the ΔJ – pH curve is completely analogous to that of the curves of the dependence of the degree of tanning of collagen by vegetable tanners on the pH, obtained by the extraction method. It is interesting to compare the absolute values of the bound tanner, obtained by both methods.

The bound tannins, determined by the extraction method, on the average are 0.5-0.6 g/g dry high substance [2,6] (e.g. in russet-tanned leather, about 57 g of tannin is bound to 100 g of albumen [2].) The data of Table 1 show that the maximum value of ΔJ (at the point of the alkaline maximum, pH 10.0) is $2.53 \cdot 10^{-4}$ and the quantity bound per g of tannin at the same pH is $5.58 \cdot 10^{-4}$, whence it follows that the observed ΔJ corresponds approximately to 0.45 g of tannin, which corresponds to 0.5 g of gelatin; consequently, the tannin bound by the gelatin at this pH is about 0.9 g/g. At pH's in the region of 6–8 we obtain, by this means, a bound quantity of about 0.5-0.6, instead of 0.3-0.4 g/g obtained by the extraction method [2, Fig.8,9]. For more accurate calculations, the distribution of the ΔJ values between tanner and gelatin must be taken into account, but if we make even the fairly probable assumption that this value is distributed proportional to the quantities of bound H^+ or OH^- ions of both components, then the results of calculation are comparatively little changed, because for the majority of points, as can be seen from Tables 1 and 2, the quantity bound by one component is considerably larger than that bound by the other. For instance, in Table 2 at pH=6.0, $\Delta J = 0.7 \cdot 10^{-4}$, and the amount of OH^- ions bound by the oak extract is $2.32 \cdot 10^{-4}$ whence the amount of tanner bound

by 0.5 g of gelatine should be $\frac{0.7}{2.32} = 0.3$ g or 0.6 g/g of gelatin. After introducing the necessary corrections for the distribution of ΔJ we obtain $0.7 \cdot \frac{2.32}{2.32 + 0.45} = 0.59$, whence $\frac{0.59}{2.32} = 0.25$ g/0.5 g of gelatin or 0.5 g/g, while the method of unextracted residues [2,Fig.8] gives for oak extract at pH=6.0, about 0.2-0.4 g/g (depending on the time of tanning). These data are of interest in that, on the one hand, they are close in order of magnitude to those derived from the literature, obtained by quite different methods and, on the other hand, they show that the actual equilibrium quantity of bound tanner is apparently considerably higher than previously assumed in accordance with the ideas outlined.

The data of Tables 1 and 2 likewise indicate the displacement of the isoelectric point of albumen towards regions of greater acidity, which is characteristic of the action of vegetable tanners; thus, for example, tannin (Table 1) displaces the isoelectric point from 5.0 to 3.6 and oak extract (Table 2) displaces it from 5.0 to 4.4, which is in complete agreement with the results obtained by other methods.

SUMMARY

On the basis of the deviation of the curves for the potentiometric titration of mixtures of gelatin and tanner from additivity, a new method of calculating the quantity of bound tanner (under equilibrium conditions) is put forward and the results are compared with previous data obtained by extracting the tanner.

LITERATURE CITED

[1] A. N. Mikhailov, Physico-Chemico Bases of the Technology of Leather. 12, 13 Moscow (1949).

[2] D. Wilson, Chemistry of Leather Production Moscow (1929).

[3] R. Page, J. Intern. Soc. Leather Trade Chem., 28, 156 (1944).

[4] K. Spiro and W. Pemsel, Z. physiol. Chem., 26, 233 (1898).

[5] O. Cohnheim and H. Kruger, Z. Biol., 40, 95 (1900).

[6] A. N. Mikhailov. Colloid Chemistry of Tannins. 288, Moscow (1935).

BLANK
PAGE

CONDENSATION OF ACETONE WITH FORMALDEHYDE[1)]

M. N. Tilichenko and A. F. Duganova

Laboratory of Organic Chemistry of the N. G. Chernyshevsky
Saratov State University

Interaction of acetone with excess of formaldehyde in weak alkali at low temperatures yields a water soluble condensation product in the form of a transparent syrup, from which there may be crystallized, after a more or less prolonged period, the anhydride of a partially known alcohol, the so-called anhydroenneaheptitol [1,2].

The other components of the syrup, in spite of their technical importance [3], have not been studied thus far since it is impossible to separate them directly by the usual methods.

In 1947, Roach and co-workers [4], showed by exhaustive allylation, that 60% of the syrup was a mixture composed predominantly of the anhydroenneaheptitol and partially of products of the lower methylolation of acetone (they were able to isolate dimethylolacetone from them with fair certainty) and 40% of it consisted of products of more complicated composition, formed, according to the ideas of the authors, as a result of the intermolecular condensation of the initially formed polyhydroxylic compound, according to the scheme:

$$CH_2OH + HOCH_2 \longrightarrow -CH_2-O-CH_2- + H_2O .$$

They based this suggestion on the fact that the average hydroxyl group content in the syrup which they obtained was only 29.2%, while in anhydroenneaheptitol the figure was 38.3% and in dimethylolacetone it was 28.8%.

In an attempt to exclude completely products of a lower degree of methylolation in the condensation of acetone with formaldehyde, we took 1 mole of acetone and 10 moles of formaldehyde (instead of 7-8 moles taken by previous investigators) and the acetone was not introduced suddenly, but drop by drop, and after the introduction of 1 ml of acetone no more was added until a negative test for acetone was obtained from the reaction mixture. By such a procedure an extremely large excess of formaldehyde was maintained right up to the end of the experiment.

One experiment was carried out in the presence of sodium hydroxide as a condensing agent, and another in the presence of barium hydroxide.

In the first case a viscous, water-soluble syrup was obtained in quantity of 334.1% relative to the acetone taken, and it contained 24.9% of hydroxide group. For quantitative formation of anhydroenneaheptitol, the yield of product should be 382.8% on the acetone taken and the OH group content should be 38.3%. Assuming further that the lowering of the OH group content by 13.4% (38.3 - 24.9) was caused by the partial self-condensation of the molecules of anhydroenneaheptitol according to the scheme shown above, we find that the

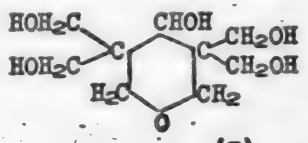
---

[1)] Communication II of a series dealing with the condensation of formaldehyde with ketones.

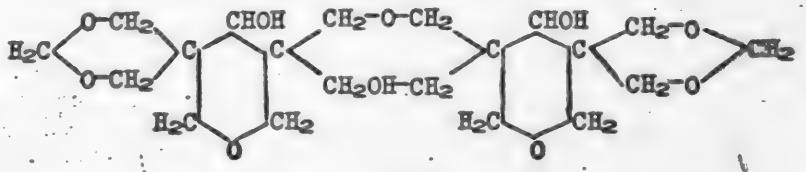
theoretically possible yield of product should be 331.5% on the acetone taken; bearing in mind that the product which we obtained can contain a certain quantity of compound of a somewhat lower degree of methylolation than in anhydroenneaheptitol, the agreement of our experimental yield with the theoretically possible one is quite satisfactory. (Attention should also be paid to the fact that residual solvents and excess formaldehyde can only be extracted from the syrup with great difficulty).

The results of the experiment with barium hydroxide were unexpected: we also obtained a substance which had the external appearance of syrup, as in the first case, (only somewhat less mobile) however in contrast with the first it easily gelatinized in water, and did not dissolve. This syrup was separated by us into the following 3 main products:

1) Water and alcohol soluble - anhydroenneaheptitol (I);
2) Insoluble in water, but soluble in alcohol - dianhydroenneaheptitol, acetalized by formaldehyde (II); and
3) Water-and alcohol-insoluble



(I)



(II)

The third product was more or less neglected but, in its properties, undoubtedly, it should belong to the same generic type as the first two and should therefore be a trianhydroenneaheptitol and may also be a mixture of polyanhydroenneaheptitols.

EXPERIMENTAL

1. Condensation of acetone with formaldehyde in the presence of barium hydroxide. For experiment we took 309 ml of 31% formalin (3.20 moles CH_2O); 18.53 g (0.32 mole) of acetone (b.p. 56-58°) and 34.17 g of powdered barium hydroxide.

In a round-bottomed flask, provided with a mechanical stirrer, a burette, (instead of a dropping funnel), a thermometer dipping into the reaction mixture, and a reflux condenser closed with a calcium chloride tube containing soda lime, the indicated quantity of formalin was introduced and 0.6 g of barium hydroxide was put in, after which acetone, in 1 ml portions, was run in through the burette slowly, drop by drop, with the stirrer working continuously and vigorously. The flask was heated on a water bath at 45-50°. The temperature of the reaction mixture during the whole time of experiment was also maintained within the limits of 45-50°.

After introducing 1 ml of acetone the supply of this liquid was interrupted and the reaction mixture was tested for the presence of free acetone (sodium nitroprusside [5]); the feed of acetone was recommenced only when a negative test was obtained for it, which required about 1 hour.

The barium hydroxide was added in portions of 0.3 g, each time a test sample showed only a weak alkaline reaction to phenolphthalein paper when dipped in the mixture.

In the course of a day (12 hours after the start of the experiment) 14.1 g of barium hydroxide was added and half the quantity of acetone required. Further addition of acetone, mixing and heating were then interrupted until the following day, on which the remaining half of the acetone and 20.07 g of barium hydroxide were introduced in the same order and under the same conditions, taking 12 hours over the process. One hour after adding the last portion of acetone the nitroprusside test gave a negative reaction, and the mixture, on cooling down to room temperature, was neutralized with 1 N H_2SO_4 (titer 0.051217); 6.4 ml were required for neutralization.

By separate titration it was established that in the neutralization, 34.17 g of the barium hydroxide which we took required 97.38 ml of 1 N H_2SO_4.

From the data obtained it follows that 5.87% formaldehyde followed the Cannizzarro-Tishchenko reaction.

The mixture, after neutralization, was a yellow homogenous liquid, with some precipitate on the bottom of the flask ($BaSO_4$).

After separating the precipitate, 192.7 ml of 1 N H_2SO_4 (titer as above), was added to the filtrate in order to precipitate $Ba^{\cdot\cdot}$ quantitatively. The precipitate, after ageing by heating for 1 hour on the water bath, was filtered off on a Buchner funnel and washed a few times with distilled water.

From the filtrate to which the washings had been added, water was distilled off at a temperature of 80° under a partial vacuum. A viscous, transparent syrup of a yellowish color remained in the flask, in quantity 68 g, which was (allowing for 5 g of excess H_2SO_4), 340% on the acetone taken. The syrup turned into a gelatinous mass on addition of water, but it did not dissolve in water; it also did not dissolve in ether or benzene; it dissolved partially in ethanol and considerably more in isoamyl alcohol.

To separate the alcohol-insoluble part, the syrup was treated with hot isoamyl alcohol and rapidly filtered through a Buchner funnel. 7 g of a transparent, very sticky mass remained on the filter; it was insoluble in water, alcohol, sulfuric ether, ethyl acetate, glacial acetic acid, benzene and carbon tetrachloride; it dissolved, on heating, in nitrobenzene.

The filtrate was evaporated under a partial vacuum on a water bath (80°) and thereafter to constant weight at 45-50° at a vacuum of 1 mm.

As a result, a thick syrup was obtained which could be drawn out into light brown threads, dissolving well in alcohol, benzene, nitrobenzene, pyridine, and insoluble in water and sulfuric ether.

Since a sample of the condensate gave a qualitative test for $SO_4^{\cdot\cdot}$ and CH_2O, 39.0 g of the substance was dissolved in 150 ml of benzene and the benzene solution was carefully washed with water. After six washings, tests for $SO_4^{\cdot\cdot}$ ($BaCl_2$) were negative; after some washings the Rimini test for CH_2O gave only a weak color which remained constant on further washing.

After distilling off the benzene (50°, partial vacuum) the residue was brought to constant weight at 45-50° and 2-3 mm. Yield 28.62 g; transparent syrup capable of being drawn into threads, straw color.

From the wash water, 3.48 g of syrup was separated; this dissolved well in alcohol and water. After 4-5 hours the syrup crystallized. After re-crystallization from alcohol the crystals melted at 155-156°.

Analysis of the Crystalline Product

0.0702 g substance: 0.1258 g CO_2; 0.0533 g H_2O.
Found %: C 48.86; H 8.35. $C_9H_{18}O_9$. Calculated %: C 48.65; H 8.10.

Determination of the molecular weight (Rast method)

0.0052 g substance: 0.0472 g camphor: Δt 20° C.
Found: M 220,234. Calculated: M 222.

Thus, the crystalline product separated can be taken to be anhydroenneaheptitol.

At this point we should turn our attention to the rate of crystallization of the syrup (4-5 hours): it is a fact that Tollens [1] found that crystallization of the syrup in some cases required 8-10 days, and in some cases weeks and months in spite of the presence of crystals of anhydroenneaheptitol prepared elsewhere).

Analysis of the basic product

0.1550 g substance: 0.3171 g CO_2; 0.1102 g H_2O
0.1534 g substance: 0.3150 g CO_2; 0.1082 g H_2O
Found %: C 55.81, 56.00; H 7.86, 7.82.
$C_{20}H_{32}O_{10}$. Calculated %: C 55.55; H 7.41.

Determination of the molecular weight

0.2038 g substance: 16.198 g C_6H_6:[1] Δt 0.156°
0.3646 g substance: 16.377 g C_6H_6: Δt 0.280°
Found: M 422.5, 416.9
$C_{20}H_{32}O_{10}$. Calculated: M 432.

Determination of OH group content (Werle)

0.1044 g substance: 22.3 ml 0.5 N NaOH
0.1985 g substance: 22.5 ml 0.5 N NaOH
control mixture: 22.5, 22.5 ml 0.5 N NaOH.

Thus, the experimental data suggests that the main product which we separated corresponds in chemical structure to II.

The absence of OH groups, as determined by Werle's method, we explain as being due firstly to the fact that secondary alcoholic groups are revealed by this method with more difficulty than primary ones and, secondly, that here no doubt some steric hindrance is encountered.

As the reaction mixture at the end of the experiment was a homogeneous aqueous solution, and the compound II separated by us was insoluble in water, then it may be suggested that in the process of condensation of acetone with an excess of formaldehyde in the presence of barium hydroxide, the main product formed is anhydroenneaheptitol (which is demonstrated by the 340% yield of condensate on the acetone taken). As a result of two successive evaporations, (initially with water and afterwards from isoamyl alcohol) in the presence of sulfuric acid, introduced by us in excess to precipitate Ba^{++}, this compound may be considered to undergo self-condensation through its alcoholic groups; acetalization of the condensed molecule is brought about by the excess of formaldehyde which remains in the syrup. It is known that acetalization occurs

[1] The cryoscopic constant of the benzene was 5.24.

very easily on contact of polyhydric alcohols with aldehydes in the presence of mineral acids (concentrated HCl, H_2SO_4).

The alcohol-insoluble substance, separated by us in quantity of 7 g from the main mass of the condensate, undoubtedly has the same generic relation to anhydroenneaheptitol as has compound II, but is a still more complex product of the intercondensation of molecules of anhydroenneaheptitol.

2. Condensation of acetone with formaldehyde in the presence of 20% sodium hydroxide. The difference between this experiment and the first was that, in place of barium hydroxide as condensing agent, 20% aqueous caustic soda, in quantity of 0.175 mole/mole of formaldehyde, was taken. The solution of alkali was introduced into the reaction mixture after each half-hour, in equal portions.

The reaction came to an end after 8 hours, i.e. it was three times as fast as in the preceding case.

At the end of the reaction, the excess of alkali was titrated with a solution of exactly 1 N HCl. 28.82% of the formaldehyde (nearly 5 times more than in the first experiment) followed the Cannizzarro-Tishchenko reaction.

The water in the neutralized reaction mixture was removed at 80° under partial vacuum. The residue was a viscous, transparent, yellow syrup. The mineral salts were extracted from the syrup by dissolving it in dry isoamyl alcohol and then filtering it. The isoamyl alcohol was removed at 80° under a partial vacuum. The residue was taken to constant weight at 40-50° and 2-3 mm.

The yield of condensate was 334.1% on the acetone taken.

The product was a viscous, transparent, yellow, syrup. It dissolved well in water, alcohol, phenol and did not dissolve in sulfuric ether, benzene, nitrobenzene or pyridine.

Determination of the OH group content by Wolff's method

0.1734 g substance: 19.10 ml 0.5 N KOH[1])
0.1886 g substance: 19.10 ml 0.5 N KOH.
Required for back titration: 14.00, 13.60 ml 0.5 N H_2SO_4.[1])
Found %: OH 25.00, 24.79 (mean 24.90).

When the syrup was mixed with benzaldehyde and concentrated HCl, a solid product was easily formed from which a crystalline compound was obtained by a triple crystallization from alcohol; in quantity it was 25% of the syrup taken, and it melted with charring at 251-253°; from elementary analysis and molecular weight the compound approximates to the bis-benzylidene ether of anhydroenneaheptitol.

Judged by the yield and by the solubility, the syrup obtained, undoubtedly, is a mixture of some products having a higher degree of methylolation of acetone, close to anhydroenneaheptitol! Its average OH group content was 24.9%, which was by 3.9% lower than dimethylolacetone, clearly showing that under the conditions of experiment obtaining, there is a partial condensation of the molecules of the polymethylol derivatives of acetone, as a result of which the OH group content is lowered. It is relevant to note that in an experiment, in which we added a smaller quantity of sodium hydroxide, we obtained in the course of 5 hours (instead of 8) a syrup containing 29.3% of hydroxyl group.

It should also be noted that, in the condensation of acetone with a large excess of formaldehyde, the formation of a Werner resin is completely excluded,

---

1) KOH and H_2SO_4 were exactly 0.5 N.

even at high temperatures (at any rate up to 100°) and using a large quantity of concentrated caustic alkali as a condensing medium. It must be borne in mind that at high temperatures and in the presence of caustic alkali, formaldehyde begins to undergo the Cannizzarro-Tishchenko at a high rate, as a result of which the excess of formaldehyde in the reaction mixture rapidly disappears and a gram molecular relationship is created, at which Werner resin is easily formed.

This fact has not as yet been duly reflected in the literature.

SUMMARY

1. It has been shown that, on evaporation of its aqueous and alcoholic solutions in the presence of a small quantity of sulfuric acid, anhydroenneaheptitol is easily converted to polyanydroenneaheptitol. If the evaporation is carried out in the presence of formaldehyde, then there is a simultaneous acetalization of the given compounds.

Compounds of this type are colorless and extremely sticky syrups, which gelatinize in water.

2. It has been shown that, in the condensation of acetone with a large excess of formaldehyde there is a quantitative formation of products of highly methylolized acetone, which indicates that there is, in the reaction mixture, a partial intermolecular condensation (with separation of water from the hydroxyl groups).

The methylolation with excess of formaldehyde is not complicated by the formation of products of the Werner resin type, even at high temperatures and when using concentrated solutions of caustic alkali as a condensing medium.

In the presence of concentrated caustic alkali the quantitative methylolation of acetone is more rapid than in the presence of barium hydroxide (in our experiments about three times faster); but, in the presence of caustic alkali, formaldehyde undergoes the Cannizzarro-Tishchenko reaction to a large extent (in our experiment about 29%) while in the presence of barium hydroxide only about 6% of the mixture reacts in this way.

LITERATURE CITED

[1] M. Appel and B. Tollens. Ann., 289, 36 (1896).

[2] Mannich and Brose, Ber., 55, 3155 (1922).

[3] I. Shaiber, Chemistry and Technology of Synthetic Resins. State Chemical Institute, 255 (1949); Ellis. Chemistry of Synthetic Resins, I, No.2, 803 (1938).

[4] R. Roach, H. Wittcoff and S. Miller, J. Am. Chem. Soc., 69, 2651 (1947).

[5] G. Meyer, Analysis and Determination of Organic Compounds, 66 (1937)

[6] G. Meyer, Analysis and Determination of the Structure of Organic Substances. Ukrainian Sci. Tech. Press, 319 (1935).

Received July 4, 1950.

DISULFO ACIDS OF CARBAZOLE

V. F. Borodkin

Ivanov Institute of Chemical Technology

In one of our papers [1] we showed that the formation of 3,6,8-carbazole-trisulfo acid from carbazole by treating it with sulfuric acid goes through the stage of the formation of carbazoledisulfo acids. The conditions of formation of the latter, and their structure, are completely unknown. The results of investigations by different authors are contradictory. Hence it appeared to us important to devote further study to this question.

According to the investigations of Schultz and Hauenstein [2], the incomplete sulfonation of carbazole by sulfuric acid monohydrate at 70-75° for 6-7 hours leads to the formation of a mixture of carbazoledi- and trisulfo acids. The sulfo chloride obtained from the disulfo acid decomposes without melting but the sulfamide melts at 222-225° with decomposition.

Schwalbe and Wolf [3] repeated the experiments under the conditions mentioned above, and likewise obtained a carbazoledisulfo acid; the sulfo chloride of the latter crystallized from acetone in the form of leaves, but the sulfamide did not melt. The potassium salt of this carbazoledisulfo acid, on heating with 48% sulfuric acid at 120°, hydrolyzed with the formation of carbazole. The same authors, by extended heating of carbazole with 67% sulfuric acid at 115°, obtained another carbazoledisulfo acid, the sulfo chloride of which melted at 102° and no sulfamide was formed. The potassium salt obtained from the disulfo acid remained unchanged when heated with 48% sulfuric acid. On the basis of these facts the authors assumed that 3 isomeric carbazole-disulfo acids exist.

Cohn [4] considers that one of these sulfo acids is carbazole-3,6-disulfo acid, because it does not form indophenol by interaction with nitrosophenol, because of blocking by the sulfo groups of the 3rd and 6th positions.

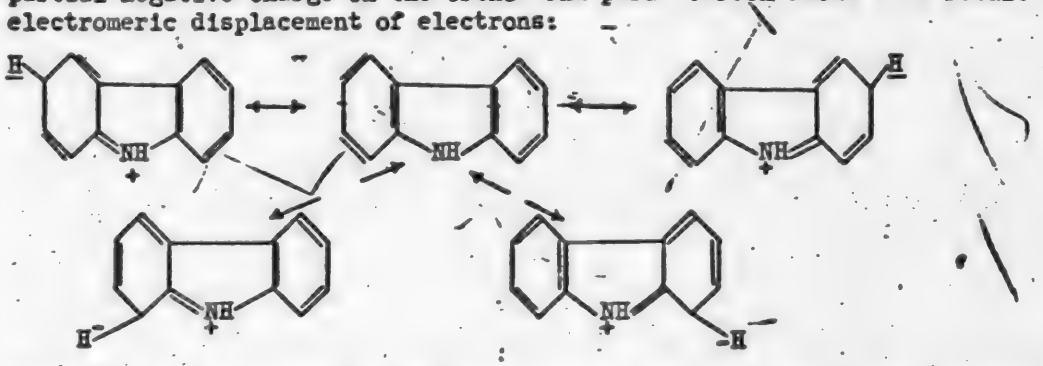
Mizuch and Gelfer [5] by acting on carbazole-3-sulfo acid with dimethyl- and diethyl sulfates, obtained the methyl and ethyl esters of carbazole-3,6-disulfo acid.

By detailed investigation of the sulfonation of carbazole with sulfuric acid monohydrate, and with dilute sulfuric acid, we obtained only 2 carbazole-disulfo acids. One of these is carbazole-3,6-disulfo acid, the other is carbazole-3,8-disulfo acid (the 3,8 and 1,6 positions are identical, hence the 3,8-disulfo acid will be called 1,6-disulfo acid).

Both the isomeric sulfo acids are formed simultaneously in the sulfonation of carbazole by sulfuric acid monohydrate. In sulfonation with dilute sulfuric acid, 1,3,6-trisulfo acid is mainly formed, together with the 3,6-disulfo acid as an impurity, in small amount. The sulfo chlorides and sulfamides of both sulfo acids have no characteristic melting point because they decompose before melting. The temperature of decomposition depends on the rate of heating, and does not give a characteristic transition point. According to our investigations, the sulfamide of carbazole-disulfo acid, with a melting point of 222-220°(with decomposition) described in the literature, is an impure mixture of the sulfamides

of two sulfo acids, and the sulfo chloride with melting point of 102° is a mixture of the sulfo chlorides carbazoledi- and carbazoletrisulfo acids. Hence the statements about the existence of 3 isomeric carbazole disulfo acids are not confirmed, the more so as the authors did not even attempt to identify the acids they obtained, by other methods, apart from the observation of the melting points of the sulfo chlorides and the sulfamides, to give a theoretical basis for the possibility of forming 3 isomeric disulfo acids.

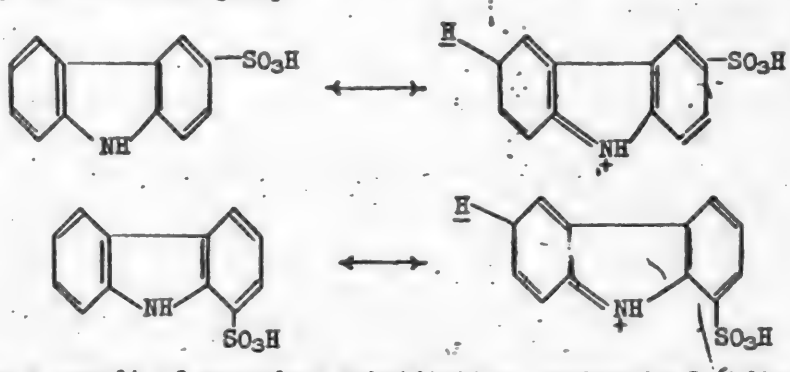
In examining the question of the entry of substituents into the carbazole nucleus (dibenzopyrrole) it is necessary to go into its structure. The imino group in the composition of carbazole, being a group of the first kind, creates a partial negative charge on the ortho- and para- carbon atoms as a result of electromeric displacement of electrons:



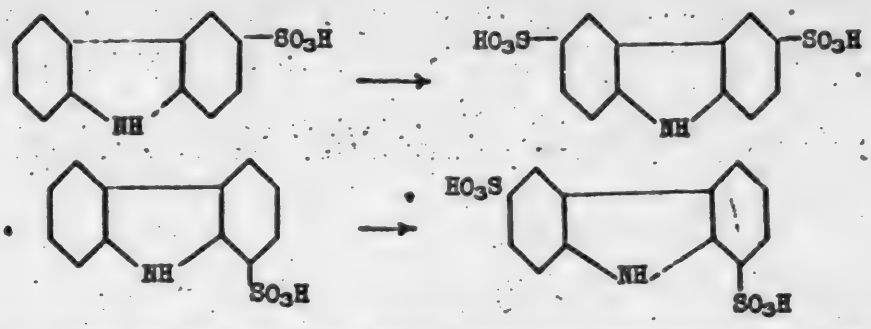
Naturally, an electrophilic reagent, such as sulfuric acid, has a directive effect. As a result of monosubstitution there should be formed carbazole-3-sulfo acid, and possibly some quantity of the isomeric carbazole-1-sulfo acid, which, however, is less probable. The possibility of substituting the sulfo group for the hydrogen of the imino group, with the formation of carbazole-N-sulfo acid (sulfamic acid) is excluded on account of the instability of the latter in acid solution.

It could be suggested that the formation of carbazole-2-sulfo acid is a consequence of the meta orientation of the quaternary, positively charged nitrogen atom, but its formation is possible only by the action of high concentration oleum on carbazole. Hence, under the conditions of sulfonation by sulfuric acid monohydrate, the hydrogen atoms in the quinogenic positions should be the first to be substituted.

The point of entry of the second sulfo group is likewise determined by the activating influence of the imino group on the quinogenic 6,8- positions of the second benzene ring, the more so since the first benzene ring is deactivated by the entry of the sulfo group.



Hence, as a result of secondary substitution, carbazole-3,6-disulfo acid and the isomeric carbazole-1,6-disulfo acid should be formed:



Even where, as a result of monosulfonation, carbazole-1-sulfo acid is partially formed, further sulfonation should lead to the formation of carbazole-1,6-disulfo acid, and not the 1,3- or 1,8-disulfo acids.

Starting from these facts, we would expect that the disulfonation of carbazole would produce a mixture of 2 isomeric disulfo acids and not 3 as has been suggested by some authors [3].

As we established in practice, the sulfonation of carbazole by sulfuric acid monohydrate at 100° results in the formation of disulfo acids, the mixture obtained consisting of carbazole-3,6-disulfo acid (70-74%) and carbazole-1,6-disulfo acid (30-26%). A similar mixture was obtained where the sulfonation was conducted at 100° with sulfuric acid monohydrate, and likewise when sulfonating carbazole-3-sulfo acid. In the first case only 50% of the carbazole was sulfonated.

These two latter facts indicate the ease of sulfonation of carbazole-3-sulfo acid to the disulfo acids and the small dependence of the orientation in the other benzene ring on the substituent entering the first benzene ring. Both benzene rings behave as though independent, and the orientation is conditioned by the imino group of the pyrrole ring. In other substitution reactions (nitrations, halogenations) the same state of affairs is found.

The formation of carbazole-1,6-disulfo acid from the sulfonation of carbazole-3-sulfo acid, also indicates that the sulfo group, entering into one of the benzene rings, leads to a partial redistribution of the electron density in the quinogenic positions of the other benzene ring. Apparently the electron density at the para-quinogenic carbon atoms is somewhat lessened, as a result of which it is possible for the sulfo group to enter into the ortho-quinogenic position.

The structure of the disulfo acids was established by preparing from them 1- and 3-aminocarbazoles through the corresponding nitro- and aminosulfo acids, with subsequent hydrolysis, and also by identification of one of the disulfo acids with synthetic carbazole-3,6-disulfo acid. The latter was obtained from 3-aminocarbazole-6-disulfo acid by diazotation, with subsequent replacement of the diazo group by the sulfhydryl group, and oxidation of the product with potassium permanganate.

EXPERIMENTAL

Sulfonation of carbazole by sulfuric acid monohydrate. 20 g of carbazole was mixed in the cold with 2 equivalents of sulfuric acid (d 1.84), the mixture was carefully stirred together, placed in a reaction container, and heated on a boiling water bath for 2 hours with periodic stirring.

The viscous liquid mass was diluted and filtered from traces of carbazole. The acid filtrate was treated with barium carbonate, the barium salts were converted

to the potassium ones and the latter were separated.

The separation was based on the different behavior of the salts to benzidine hydrochloride and their different solubilities in ethyl alcohol. Carbazole-3,6-disulfo acid does not dissolve in alcohol, gives a water-insoluble salt with benzidine hydrochloride and can be practically quantitatively separated from the isomeric carbazole-1,6-disulfo acid, which dissolves in alcohol and does not give a water-insoluble salt with benzidine hydrochloride.

By repeated treatment of the mixture of the potassium salts of the disulfo acids with ethyl alcohol at the boil, with subsequent prolonged treatment of the alcohol-insoluble precipitate with benzidine hydrochloride, we obtained the pure potassium salt of carbazole-3,6-disulfo acid, and from the alcoholic solution, carbazole-1,6-disulfo acid.

Analysis of the potassium salts of the sulfo acids obtained for their potassium content gave positive results.

Potassium salt of carbazole-3,6-disulfo acid, separated from the residue insoluble in alcohol:

0.1351 g substance: 0.0591 g K_2SO_4.
Found %: K 19.59.
$C_{12}H_7N(SO_3K)_2$. Calculated %: K 19.36.

Potassium salt of carbazole-1,6-disulfo acid, separated from alcoholic solution:

0.1436 g substance: 0.0626 g K_2SO_4.
Found %: K 19.49
$C_{12}H_7N(SO_3K)_2$. Calculated %: K 19.36.

It is impossible to obtain pure carbazole-1,6-disulfo acid by separating the sulfo acid with benzidine hydrochloride alone.

From the disulfo acids obtained the sulfo chlorides were prepared, which on heating decomposed, and did not melt; the temperature of decomposition depended on the rate of heating. Thus, for the sulfo chloride of carbazole-3,6-disulfo acid the temperature of decomposition was found to be 132 and 138°, for carbazole-1,6-disulfo acid it was found to be 127 and 140°, for the sulfamide of carbazole-3,6-disulfo acid, 220 and 230°, and for carbazole-1,6-disulfo acid 235 and 250°. Consequently, it is not possible to characterize the disulfo acids by the temperatures of decomposition of their sulfo chlorides and sulfamides.

The sulfo chlorides were obtained by acting on the potassium salts with phosphorus pentachloride, alone or mixed with phosphorus oxychloride, for 35-40 minutes on a boiling water bath, with subsequent transfer to cold water; the product after washing and drying was subjected to analysis.

Sulfo chloride of carbazole-3,6-disulfo acid:

0.1360 g substance: 0.1130 g AgCl
0.1532 g substance: 0.1891 g $BaSO_4$.
Found %: Cl 20.45, S 16.92
$C_{12}H_7N(SO_2Cl)_2$. Calculated %: Cl 19.50, S 17.58

Sulfo chloride of carbazole-1,6-disulfo acid:

0.1560 g substance: 0.1250 g AgCl.
0.1532 g substance: 0.1896 g $BaSO_4$.
Found %: Cl 19.96, S 16.99
$C_{12}H_7N(SO_2Cl)_2$. Calculated %: Cl 19.50, S 17.58

The sulfo chlorides are insoluble in cold water, but dissolve well in alcohol, acetone, and ethyl acetoacetate, poorly in benzene, toluene, and chloroform. When the sulfo chlorides were introduced into an aqueous ammonia solution in the cold they dissolved, producing a green coloration, but the sulfamides could not be separated.

The sulfamides were obtained by passing dry ammonia into a solution of the sulfo chloride in ethyl acetoacetate, until precipitation ceased, followed by filtration and washing of the precipitate with acetone. The sulfamides dissolve well in water and poorly in organic solvents.

Sulfonation of 20 g of carbazole with 1 equivalent of sulfuric acid (d 1.84) at 100° left 10 g of carbazole unattacked. From the mixture of sulfo compounds there was also separated two carbazole-disulfo acids identical with those produced by the sulfonation of carbazole with 2 equivalents of sulfuric acid. Experiments were made on the sulfonation of carbazole under the conditions described by Schultz and Hauenstein (sulfonation with 1 equivalent of d 1.84 sulfuric acid at 70-75° for 7 hours). From the mixture of sulfo compounds obtained, after separating the unchanged carbazole, we obtained the potassium salts and from them the sulfo chlorides and sulfamides; the latter decomposed, without melting, at 220-250° (depending on the rate of heating). Carbazole-3,6- and 1,6-disulfo acids were also obtained from the potassium salts, by treatment with alcohol.

Thus the melting point of 222-225°, quoted in the literature for a sulfamide, relates to the product from a mixture of carbazole-disulfo acids.

Sulfonation of carbazole by weak sulfuric acid. The sulfonation of carbazole with dilute sulfuric acid was undertaken in order to obtain carbazole disulfo acids and to identify them with the sulfo acids, formed in the sulfonation of carbazole by sulfuric acid monohydrate. The sulfonation was carried out under the conditions described by Schwalbe and Wolf [3], by heating carbazole with a large excess of 67% sulfuric acid, at 115° for 10 hours. As we showed earlier [1], under these conditions a considerable quantity of the trisulfo acid is formed; the separation of the trisulfo acids from the disulfo acids is difficult. The benzidine separation method which we employed was not very successful with large concentrations of trisulfo acid, since the latter interfered with the precipitation of the benzidine salts of the disulfo acids. Hence, the mixture of sulfo compounds was treated initially with potassium chloride, the mixture of sulfo acids was subjected to fractional crystallization from water, as a result of which the trisulfo acid remained in the mother liquors, and afterwards the disulfo acids were further purified by the benzidine method. As analysis showed, this method of purification makes it possible to obtain pure potassium salts of a carbazoledisulfo acid.

0.1511 g substance: 0.652 g K_2SO_4.
Found %: K 19.32
$C_{12}H_7N(SO_3K)_2$. Calculated %: K 19.36

The separated potassium salt of the carbazole-disulfo acids does not give a coloration with chloranil in sulfuric acid, with benzidine hydrochloride it gives a water-insoluble benzidine salt, which does not dissolve in alcohol. In its properties it is identical with the salt of carbazole-3,6-disulfo acid.

The sulfo chloride obtained from the disulfo acid, before purification by the benzidine method, began to decompose at 98-105°. The same compound, after purification by this method, commenced to decompose at 130-132°. In both cases the decomposition temperature depends on the rate of heating. The melting point of 102° for the sulfo chloride, mentioned in the literature, is thus not charac-

teristic but erroneous. It should also be mentioned that when the disulfo acids obtained are heated with 10% sulfuric or hydrochloric acid in a closed tube at 170° they hydrolyze with separation of carbazole.

Thus, the sulfonation of carbazole with sulfuric acid monohydrate leads to the formation of the 1,6- and 3,6-disulfo acids, and in sulfonation with weak sulfuric acid, apart from carbazoletrisulfo acid, carbazole-3,6-disulfo acid is also formed.

The structure of the disulfo acids obtained was established by preparing aminocarbazoles from them. For this purpose they were nitrated, the nitro acids were reduced and the aminosulfo acids were hydrolyzed. The hydrolysis products obtained were identified with the 1- and 3-aminocarbazoles described in the literature.

The nitro derivatives of both disulfo acids crystallized with 3 molecules of water and contained 1 nitro group. The quantity of nitro group was determined by reduction of an exactly weighed quantity of the nitro compound, and subsequent titration of the reduced solution with sodium nitrate in acid.

The reduction of the nitro-disulfo acid to the aminodisulfo acid was usually effected by iron turnings in acid; the sulfo acid was separated after precipitation of the iron, in the form of a sodium salt.

The free carbazole aminosulfo acids dissolved poorly in water, oxidized rapidly in the air and were violet. The aminosulfo acids were hydrolyzed with 20% HCl in a closed tube at 175-180° for 5 hours. As a result, aminocarbazoles with melting points of 185-196° and 256° were obtained.

The melting point given in the literature for synthetically prepared 1-aminocarbazole is 195° [5], and for 3-aminocarbazole it is 254° [6].

Since the disulfo acid of carbazole is soluble in alcohol, it does not give a salt with benzidine hydrochloride, and shows a color reaction with chloranil in acid, from which we obtained 3-aminocarbazole, which we consider to be carbazole-1,6-disulfo acid. The disulfo acid isomeric with it, giving 1-aminocarbazole, appears to be carbazole-3,6-disulfo acid. It must be mentioned that 1-aminocarbazole was also obtained from the carbazole-3,6-disulfo acid which we synthesized. Attempts to obtain the methyl and ethyl esters of the sulfo acids were not successful.

Properties of the disulfo acids. The potassium and sodium salts of carbazole-3,6-disulfo acid dissolve well in cold and hot water, the barium and calcium salts somewhat less so; the salts are insoluble in organic solvents. A benzidine salt is obtained by acting on the salts with benzidine hydrochloride; this is not soluble in hot water, and melts with decomposition. By acting on the potassium or sodium salt with phosphorus pentachloride, the disulfo chlorides are formed, melting with decomposition.

Carbazole-3,6-disulfo acid does not give a color reaction with nitrosophenol and chloranil in sulfuric acid; in air, it rapidly turns blue.

The salts of carbazole-1,6-disulfo acid dissolve well in hot and cold water; the potassium and sodium salts dissolve in hot ethyl alcohol. Benzidine hydrochloride does not yield a benzidine salt with them. A blue coloration is obtained with chloranil and nitrosophenol in sulfuric acid, indicating the presence of free positions para to the imino group.

A sulfo chloride, melting with decomposition, is formed by the action of phosphorus pentachloride on the potassium or sodium salts.

SUMMARY

1. Statements about the existence of 3 isomeric carbazoledisulfo acids, obtained by sulfonation of carbazole, and based on the melting point of the sulfochlorides and sulfamides are erroneous, since the melting point of the latter, given in the literature, cannot be substantiated. Carbazoledisulfo acids cannot be characterized by the melting points of the sulfo chlorides because the latter decompose on heating.

2. It has been shown that, on sulfonating carbazole with sulfuric acid monohydrate (1 or 2 equivalents), 2 isomeric disulfo acids are formed. By converting them to aminocarbazoles, it was established that in one of them the sulfo groups are in the 1,6-positions, and in the other they are in the 3,6-positions.

3. The carbazoledisulfo acid, obtained by sulfonating carbazole with weak sulfuric acid, is identical with one of the sulfo acids formed in sulfonation with sulfuric acid monohydrate, and appears to be the 3,6-disulfo acid.

LITERATURE CITED

[1] V. Borodkin and T. Malkova, J.Appl.Chem. 21, 849 (1948).

[2] G. Schults and Hauenstein, J.prak.Chem., N.F., 76, 336 (1907).

[3] Schwalbe and Wolf, Ber., 44, 236 (1911).

[4] G. Cohn. Die Carbazolgruppe. Leipzig (1919).

[5] K. Mizuch and Ts. Gelfer, J. Gen. Chem., 17, 823 (1947).

[6] P. Eikhman, V. Lukashevich and E. Silaeva, Industrial Organic Chemistry, 6, 93 (1939).

Received November 28, 1950

BLANK
PAGE

BRIEF COMMUNICATIONS

RATE OF SYNTHESIS OF SODIUM FORMATE

G. D. Sirotkin

Ivanov Institute of Chemical Technology

The technical synthesis of sodium formate is a heterogeneous process, in which carbon monoxide interacts with solid caustic soda; $NaOH + CO \longrightarrow HCOONa$. In spite of the fact that the process has been in use in industry for more than half a century, so far no determinations of its kinetics have been attempted. Only the old work of Berthelot [1], Merz and Tibirace [2] is known, indicating that the completely dry substances do not interact with one another, that elevated temperatures and carbon monoxide pressures act positively on the reaction, and that the reaction can also be accelerated by introducing small additions of alcohol, ether and acetone.

The reaction is accompanied by a whole series of extremely interesting phenomena, which have still not been properly noted in the literature. Among these phenomena the existence of a certain induction period is of considerable practical importance; the extent of this induction period, as experiment has shown, can be shortened by the addition of sodium formate to the caustic soda, which shows that the synthesis has an autocatalytic character.

In view of the practical importance of the question and the absence of any literature relating to it, we undertook a series of laboratory experiments in order to find out the effect of additions of formate to caustic soda on the rate of synthesis.

EXPERIMENTAL

The experiments were carried out in a special set-up according to the following scheme.

100% carbon monoxide from a gasometer was passed through a heater at a definite rate and then through the reaction vessel, in which a weighed quantity of freshly prepared mixture of caustic soda and sodium formate had been placed on a grid. In passing through the layers of mixture, the carbon monoxide partially entered into combination and at the same time created in the reaction zone a gas atmosphere of constant composition. The excess gas passed out through a liquid seal. To maintain the desired temperature, the reaction vessel was immersed in a bath of liquid boiling at a constant temperature.

For making up the charge, technical caustic was used, consisting of NaOH (88.32%), Na_2CO_3 (7.65%) and H_2O (4.03%), and technical sodium formate containing HCOONa (91.37%), Na_2CO_3 (5.54%) and H_2O (3.09%).

At the end of the experiment, the contents of the reaction vessel were extracted by dissolving and were analyzed.

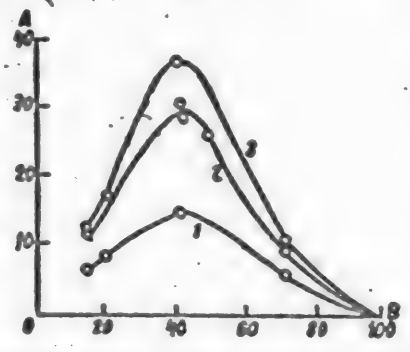
The analysis of the formate was made according to State Standard No. ST-27 5946, according to which sodium formate is oxidized in alkaline permanganate, which is afterwards reacted, in acid solution, with an excess of oxalic acid, and the latter is back-titrated with permanganate.

The results of the experiments, set forth in Table 1, show that the yield of formate depends on the formate content in the original charge (see Fig.).

Table 1

Dependence of the Yield of Formate on the Duration of Synthesis at 140°, and on the Initial Mixture Composition

Duration of synthesis (in hours)	Initial charge contained				Increase in formate content	
	NaOH		HCOONa		(in g)	(In % of the sum NaOH + HCOONa)
	(in g)	(in %)	(in g)	(in %)		
2	4.53	72.58	0.86	13.79	0.36	6.0
2	3.89	64.50	1.20	20.00	0.40	8.0
2	2.91	41.70	2.89	41.30	0.85	14.8
2	0.84	13.40	4.48	71.20	0.29	5.6
4	4.73	92.6	-	-	0.48	10.0
4	4.24	72.58	0.81	13.79	0.53	10.6
4	3.41	41.68	3.39	41.35	2.04	30.0
4	2.62	44.9	2.46	42.20	1.42	28.4
4	1.39	41.5	1.66	49.50	0.78	26.0
4	0.88	13.4	4.70	71.20	0.506	9.0
6	4.61	72.58	0.88	13.79	0.64	11.6
6	3.44	64.50	1.07	20.50	0.76	17.0
6	2.86	41.68	2.83	41.30	2.07	36.3
6	0.96	13.35	5.13	71.20	0.60	10.0



Dependence of the increase of formate on the composition of the charge. A) Increase in formate (in % on weight of charge); B) HCOONa content in the charge (in %). Time (in hours). 1 - 2; 2 - 4; 3 - 6.

The rate of synthesis of formate increases with increase in concentration of formate in the initial charge, attains a maximum when the quantities of caustic and formate are approximately equimolecular and afterwards, with further increase in the formate concentration, falls off. Consequently, in the heterogeneous process for the synthesis of formate, represented by the usual chemical equation $NaOH + CO \longrightarrow HCOONa$, the formate takes an active part, i.e., at any stage of this heterogeneous process the presence of formate facilitates matters.

It may be supposed that the positive role of the formate on the process of its own synthesis and the autocatalytic character of the latter is connected with the existence, noted earlier [3], of a compound of formate with caustic ($HCOONa \cdot NaOH$) and that carbon monoxide is more easily adsorbed on this compound than on caustic soda. Thus the industrial synthesis of the formate may be represented by the following schemes:

1) $NaOH + CO \rightarrow HCOONa$ (slow reaction);

2) $HCOONa + NaOH \rightarrow HCOONa \cdot NaOH$ (intermediate state);

3) $HCOONa \cdot NaOH + CO \rightarrow 2HCOONa$ (more rapid reaction).

It is seen that to ameliorate the synthesis it is necessary to facilitate the attainment of the active state of the charge which may be ensured by fairly

close contact between the solid particles of formate and caustic (mixing) and by adjusting the temperature to that at which the crystal lattice softens, which facilitates the penetration of atoms of one substance into the lattice of the other; according to information in the literature [4] this temperature is about 120° (the temperature of reaction is equal to about 0.8 of the melting point of HCOONa).

Under the conditions of our experiments, involving synthesis with undisturbed charges, without mixing the active state of the charge was created during the period of preliminary stirring together, and during the prior heating of the mixture to the reaction temperature before passing the carbon monoxide over it. Hence, it may be taken that the active surface and quantity of active centers, determined by the presence of the compound HCOONa·NaOH, was largest at the beginning of the reaction and decreased as the synthesis progressed. The magnitude of the active surface, with insufficient formate in the charge, should be proportional to the content of the latter, and with excess of formate it should be limited by the caustic content.

When the pressure of the carbon monoxide, the temperature and state of subdivision of the charge are constant, the rate of synthesis will be a function only of the HCOONa·NaOH content in the charge and can be expressed by the equation

$$\frac{dx}{d\tau} = K(a_n - x)$$

where K is the rate constant; a_n is the formate content in the initial charge with insufficient formate, and the caustic content in the charge with excess of formate; x is the quantity of newly-formed formate.

After integrating, the following equation is obtained:

$$K = \frac{1}{\tau} \log \frac{a_n}{a_n - x}$$

Inserting into this equation the rate constants for the synthesis, we obtained the following values (Table 2).

Table 2

Values of the Rate Constants for Different Charge Compositions and Different Times of Synthesis

Duration of experiment (in hours).....	2	2	2	2	4	4	4	6	6	6	6
Concentration of HCOONa in the charge (in %)....	13.79	20.0	41.3	71.2	13.79	41.3	71.2	13.79	20.5	41.3	71.2
Reaction rate constant.....	0.12	0.09	0.06	0.05	0.115	0.10	0.045	0.093	0.091	0.093	0.033

As can be seen from Table 2, the rate constants for all values of the HCOONa concentration, except when this is very high (71.2%) show pretty satisfactory agreement for such a complex multi-stage process. The considerable diminution, by approximately two-fold, of the rate constants with large excess of formate, can be explained by the fact that by grinding the formate and caustic together, the softer formate grinds to a finer powder and surrounds the particles of caustic, as a result of which the synthesis of formate is made more difficult, since the carbon monoxide has to diffuse through this coating.

SUMMARY

1. Addition of formate to caustic accelerates the synthesis of the former; the accelerating effect of formate addition on the synthesis increases right up to equivalent ratio of formate to caustic in the mixture.

2. The autocatalytic character of the synthesis of formate is bound up with the absorption of carbon monoxide more easily on the compound HCOONa·NaOH than on pure NaOH.

LITERATURE CITED

[1] B. N. Dolgov. Methods of Chemical Utilization of Carbon Monoxide (1936).

[2] Merz and Tibirace, Ber., 13, 23 (1880).

[3] Barzakovsky. Nature. 4, 13 (1943).

[4] Sirotkin. J. Appl. Chem. 23, 3, 275 (1950). [1)]

Received November 21, 1950.

[1)] See Consultants Bureau English translation, p. 285.

RESISTANCE OF THE ELECTROLYTE IN A BATH WITH CYLINDRICAL ELECTRODES

A. D. Ershov and V. S. Aforshin

Theoretical calculations of the resistance of the electrolyte in baths used for the electrolysis of salts, as a function of the configuration of the electrodes, is in general a difficult task. At present, some formulas are known for the resistance, obtained with certain simple combinations of electrodes of regular form [1-3].

The results of the calculations presented in this paper supplement the known theoretical formulas by another formula, expressing the dependence of the resistance of the electrolyte in the bath on the dimensions, and the mutual disposition of a cylindrical anode and of systems of cylindrical cathodes, disposed symmetrically relative to the anode.

The configurations of the electrodes in such a cell, as has been shown by us, is quite satisfactory from the practical point of view. In the given case the replacement of the cylindrical cathode in cells by two co-axial cylindrical electrodes, with a " lattice work" cathode (system of cylindrical cathodes) corresponds completely with the practical necessity for perforated solid cathodes, since it leads to a considerable increase in the working surface and consequently to a decrease of the current density and of the cathode polarization.

Method of calculation. A metallic cylindrical electrode of h (height of immersed portion) is immersed vertically into an electrolyte with a specific resistance ρ. In the center is placed a cylinder of radius r_1 (anode) and symmetrically around it are disposed n cathodes, joined together into an external ring of cathodes of identical radius r_2.

The distance between the axis of the anode and the axis of any of the n cathodes is equal to l. It is required to determine the true ohmic resistance of such a system.

Since in the steady state, the distribution of the lines of current flow between the electrodes in the bath agrees with the distribution of the lines of force in a static problem (positive charge $+\gamma$ on the internal cylinder and the negative $-\frac{\gamma}{n}$ on each of the external cylinders), then the electrical potential φ and the electric field stress E, necessary for the solution of the problem, can be found by the usual electrostatic methods, thus replacing our problem by the equivalent static problem. The equality of all the cathode cylinders permits us to consider separately the resistance of the electrolyte between the anode and one of the cylinders of the cathode and to divide the results obtained by n. The resistance of the electrolyte between the chosen pair of electrodes may be easily found from the difference of potential U between the electrodes and the current strength I between them, $R = \frac{U}{I}$.

The current strength we find by integrating the current density $J = \frac{1}{\rho} E$. of the electrolyte (height h, over the angle $\frac{2\pi}{n}$ covered by each cylinder of the cathode).

Thus, for solving the problem it is necessary to know the potential difference U and the electric field stress E at any section of the electrolyte between the electrodes. Both of these may be found from the equivalent static case.

$$U = 2\gamma \ln \frac{(1-r_2)\sqrt[n]{(1-r_1)}}{r_1\sqrt[n]{r_2}} \qquad (1)$$

and likewise for the points of a plane perpendicular to the line joining the centers of the anode and the cathode and passing through their middle:

$$E = 2\gamma \frac{\sqrt{x^2(n-1)^2 + nl^2}}{nx^2} \qquad (2)$$

where x is the distance of a point on this plane from the axis of the cylindrical electrodes.

The temporary introduction of the magnitude of the static charge similarly leads to the values of U and I and shortens the calculation of the resistance R.

Results of calculations. Leaving out the simple but rather voluminous calculations, we arrive finally at a formula for the complete resistance of the electrolyte in our cell:

$$R = \frac{\rho \ln\left(\frac{1-r_2}{r_1}\sqrt[n]{\frac{1-r_1}{r_2}}\right)}{4h\left[\frac{n-1}{2}\ln\frac{(n-1)^2\log\frac{\pi}{n} + \sqrt{(n-1)^2\tan^2\frac{\pi}{n} + (n+1)^2}}{n+1} + \sqrt{n}\arctan\frac{2\sqrt{n}\tan\frac{\pi}{n}}{\sqrt{(n-1)^2\tan^2\frac{\pi}{n} + (n+1)^2}}\right]} = \frac{\rho}{h} \cdot A_1. \qquad (3)$$

It is natural to compare this expression with the formula for the resistance of an electrolyte in a bath with two coaxial cylindrical electrodes [1]:

$$R = \frac{\rho \ln \frac{l}{r_1}}{2\pi h} = \frac{\rho}{h} A_2 . \qquad (4)$$

(The meaning of the symbols in (4) is the same as in our expression).

It should be noted in particular that Formula (3) which we have obtained transforms into Formula (4), as the radius of the cylinders of the cathode $r_2 \to 0$ and the number of the cylinders $n \to \infty$. This is a complete check on the correctness of the calculation.

Investigation shows that beginning approximately with $n = 30$, the second term in the denominator is less than 0.1 of the first term. Hence, for practical purposes we may use the following approximate formula:

$$R = \frac{\rho \ln\left(\frac{1-r_2}{r_1}\sqrt[n]{\frac{1-r_1}{r_2}}\right)}{2h(n-1)\ln\frac{(n-1)^2\tan\frac{\pi}{n} + \sqrt{(n-1)^2\tan^2\frac{\pi}{n} + (n+1)^2}}{n+1}} \qquad (5)$$

For comparing the values of the electrolyte resistance in our cell and in a cell with two coaxial cylindrical electrodes, we have calculated the values of the factors A_1 and A_2 in Formulas (3) and (4), which must be multiplied by $\frac{\rho}{h}$ to give the complete resistance of the cells of two different types.

With $r_1 = 30$ cm and $l = 40$ cm, $A_2 = 4.58 \cdot 10^{-2}$. For these values of r_1 and l, A_1 has the values:

For $r_2 = 1$ cm and $n = 50$ $A_1 = 4.93 \cdot 10^{-2}$
$r_2 = 1$ cm and $n = 100$ $A_1 = 4.62 \cdot 10^{-2}$
$r_2 = 2$ cm and $n = 50$ $A_1 = 4.30 \cdot 10^{-2}$

In general it should be noted that the resistance R from Formula (3) does not depend very much on n or r_2. There is a much greater dependence of R on the radius of the anode r_1 and on the distance l between the axes of the cylinders of the anode and cathode.

SUMMARY

1. A theoretical formula for the resistance of an electrolyte of a cell, having a cylindrical anode and a system of cylindrical cathodes disposed symmetrically around it (axes of all these electrodes parallel) has been obtained.

2. It has been calculated that, in the practically important cases the resistance of such a cell differs only a little from the resistance of a cell with two coaxial cylindrical electrodes.

3. A considerable decrease of the current density on the surface of the cathode should notably lower the cathode polarization and for the same reason should increase the current efficiency.

LITERATURE CITED

[1] K. A. Krug. Bases of Electrotechnics. 57 (1936).

[2] V. P. Mashovets and V. M. Berenblit. Trans. All Union Al-Mg. Inst. 19, 188 (1939).

[3] V. P. Mashovets, V. V. Cherdyntsev and M. V. Neustrueva, J. Appl. Chem. 20, 660 (1947).

Received October 30, 1950.

BLANK
PAGE

ACCELERATED METHOD OF OBTAINING LEAD OXIDE

F. P. Shalaikin

Lead oxide is widely used in glass, earthenware and paint production and also in analytic chemistry.

The present methods of preparing lead oxide differ in their complexity and duration [1,2]. This raises the question of working out a rapid method for obtaining this oxide.

In our work we have investigated the conditions for the formation of lead oxide by heating pure metallic lead with chemically pure ammonium and potassium nitrates. It was established, by a preliminary series of experiments, that the formation of PbO by the action of potassium nitrate on lead is extremely slow, and does not go to completion. This is explained by the fact that the surface of contact of the oxygen atoms, liberated by the molten KNO_3, with the particles of molten lead is not large enough.

It was established experimentally that on heating ammonium nitrate with molten lead no oxidation occurs. The reacting mass in the crucible was initially converted to a viscous, and afterwards to a dry, cement-like, mass. But if, to a definite weight of molten lead, the calculated quantity of potassium nitrate is added and afterwards small portions of ammonium nitrate are introduced gradually into the molten mass, the formation of oxide is considerably increased. Analysis gave the following results (average of three determinations); 5 g Pb oxidized in 12 minutes, 15 g in 22 minutes, 25 g in 29 minutes, and 35 g in 41 minutes. The cause of the acceleration of the reaction appears to be that, in proportion to the amount of ammonium nitrate added, the mass in the crucible gradually thickens, breaks up and increases in volume. The phenomenon is characterized by a decomposition of ammonium nitrate at high temperatures, into water and nitrous oxide which breaks up the reacting mixture. The surface of the particles of KNO_3, contiguous with the particles of molten lead, increases as a result, and the formation of PbO is considerably accelerated.

If ammonium nitrate is initially added to molten lead and afterwards small portions of potassium nitrate are introduced, then the final result is the formation of lead oxide but the reaction is slower and uses up a larger quantity of KNO_3 and NH_4NO_3.

A weighed quantity of chemically pure lead is placed in an iron crucible or basin of 50-75 ml capacity (the usual porcelain crucibles are attacked), and heated over a burner flame until it melts; at this point, small portions, 0.1-0.2 g of potassium and ammonium nitrate are added in turn. The mass in the crucible should be friable and should be stirred all the time with an iron or hard glass spatula (if the reacting mass begins to solidify KNO_3, or in cases where much of it is present, NH_4NO_3 should be added).

The end of the reaction is detected by the absence of fine particles of free lead on examination with a 10× magnifying glass. The lead oxide obtained is washed, with slightly heated distilled water, on a Buchner funnel, to remove unreacted potassium and ammonium nitrate and the potassium nitrite formed. The progress of washing is followed with diphenylamine, which demonstrates the presence of nitrates, and with a solution of potassium permanganate, to show the presence of nitrites in the wash water.

After washing the lead oxide it is sucked dry on a Buchner funnel and dried in an oven at 100-110° and ground to powder.

We give the average results of analysis from 3 determinations:

Quantity of KNO_3 (in g)	Quantity of NH_4NO_3 (in g)	Weight of Pb (in g)	Time of oxidation of Pb (in min)
3	5	5	9
9.6	16	15	16
16	24	25	21
22	34	35	29

It should be noted that the introduction of KNO_3 in excess dilutes the reaction mixture, and the formation of lead oxide slows down. Excess of NH_4NO_3 thickens the mass in the crucible to the solid state, and this may also slow down the rate of reaction. A more intense oxidation goes on when the mass in the crucible is maintained in the semi-liquid friable condition.

On addition of a small quantity (0.1-0.2 g) of potassium nitrate to molten lead, its degree of oxidation in the presence of ammonium nitrate is raised. This increases the rate of the formation of PbO, shortens the time of analysis and diminishes the quantity of potassium and ammonium nitrates consumed.

LITERATURE CITED

[1] Reformatsky. Inorganic Chemistry, 15th edn. 453-456 (1929).

[2] Yu. V. Karyakin. Pure Chemical Reagents (1936).

Received June 20, 1949.

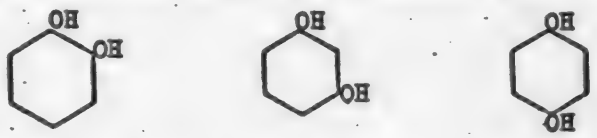
COLORIMETRIC DETERMINATION OF SMALL QUANTITIES OF DIHYDRIC PHENOLS

D. N. Vaskevich and Ts. A. Goldina

All Union Research Institute for Labor Protection
All Union Central Council of Trade Unions, Moscow

In the practice of organic analysis wide use is made of colorimetric reactions which permit isomers to be differentiated from one another; these reactions also permit the determination of small quantities of substance. It is natural, therefore, to try to use colorimetric reactions for the quantitative determination of isomers.

We have attempted to do this for the dihydric phenols: pyrocatechol, resorcinol, and hydroquinone, having the following structures:



These substances are widely used in organic synthesis and in the dyestuffs industry, and a method of determining small quantities of them would be of great value both for investigations and for practical purposes – for example, for technical analysis, for the evaluation of the state of the atmosphere in the corresponding plants, etc.

In technical analysis, the bromide-bromate method [1] is used for the determination of dihydric phenols. A method for the determination of resorcinol in admixture with phenol is known, based on the nitrosification of the mixture of phenols and determination of the final titer with an external indicator – starch iodide paper [2]. Cerimetric titration with ferrous phenanthroline as an indicator is used; this method is more accurate than iodometric titration.

Of the micro methods of determining dihydric phenols we note the colorimetric determination of hydroquinone, based on the formation of a colored complex with phosphomolybdic and phosphotungstic acids [3], and the colorimetric determination of pyrocatechol with an aqueous solution of ferrous sulfate, to which Rochelle salt has been added [4].

We set ourselves the aim of working out a colorimetric method for the quantitative determination of small quantities of dihydric phenols. The use of one of these reactions would permit the elucidation of the ratio between different isomers. For this purpose we fixed on the reaction of dihydric phenols with ammoniacal solutions of cadmium sulfate as being more sensitive than, for example, the reaction with ferric chloride.

Depending on the medium, each of the dihydric phenols gives a characteristic color of solution (Table 1).

We carried out the reaction in water as being more convenient than alcohol or ether. The color of the solution and the character of its formation is so individual for each phenol that it permits a specific answer to be given to the

question of which phenol is present.

In carrying out the reaction by the method we have worked out (see below) there is a limit of detection and the accuracy of the determination is as follows:

	Hydroquinone	Resorcinol	Pyrocatechol
Accuracy of determination (in mg)	0.01	0.005	0.01
Detection limit (in mg/4 ml)	0.005	0.002	0.005

EXPERIMENTAL

Method of analysis. To 4 ml of an aqueous solution of the dihydric phenol, 0.05 ml of 0.1 N ammoniacal solution of cadmium sulfate is added.[1] Since the ammoniacal cadmium complex dissociates relatively easily [6] ($K = 1.0 \cdot 10^{-7} - 3.8 \cdot 10^{-7}$) after it has been added to the solution, a small turbidity is formed. In order to eliminate this, 0.1 ml of a 25% ammonia solution is added immediately; the color then commences to form immediately, being characteristic for each phenol.

Table 1

Dependence of the Reaction Product Color on the Solvent

Solvent	Phenol			Literature
	Pyrocatechol	Resorcinol	Hydroquinone	
Ether	-	Yellow, then blue, then green	-	[5]
Alcohol	Granite-red	Green	Yellow, then brownish-red	[5]
Water	Pale yellow	Straw yellow	Yellow-pink then yellow-brown	our work

Hydroquinone gives a yellow-pink color, turning after 5 minutes to yellow-brown. Resorcinol gives a straw-yellow color, the intensity of which develops very slowly; the maximum intensity is only obtained after 15-17 hours. Pyrocatechol gives a very weak yellow color, the maximum intensity of which is obtained after 15 minutes. The determination of the phenols content is made by comparing the color of the test solution with that of a standard series, prepared simultaneously with the test solution and treated exactly like it.

We established that the most accurate results were obtained with hydroquinone 10 minutes, with resorcinol 30 minutes and pyrocatechol 15 minutes after the addition of the reagent.

As the result of a series of experiments, we established that the most suitable standard series was obtained with the following dihydric phenol contents in 4 ml of solution:

For hydroquinone.....0, 0.01, 0.02, 0.04, 0.06, 0.08, 0.010 mg;
For resorcinol .....0, 0.0057, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08 mg;
For pyrocatechol.....0, 0.02, 0.04, 0.06, 0.08, 0.10, 0.12, 0.14, 0.16 and 0.18 mg.

1) The ammoniacal solutions of cadmium sulfate are prepared from 0.1 N $CdSO_4$ by adding to it, dropwise, 25% ammonia until the turbidity formed disappears. The solutions should be completely transparent.

All experiments were carried out with crystallized substances having melting points in agreement with those in the literature. In certain cases, we analyzed the unrecrystallized product in parallel (this is specified in the relevant places in this paper).

In the tables below are given the average values of 3-6 experiments. The maximum deviation from the average was usually not more than 10-15%.

Determination of hydroquinone. Results of the analysis of this substance are given in Table 2.

Table 2

Determination of Recrystallized Hydroquinone

Taken (mg)	Found (mg)	Found (%)
0.000	0.000	-
0.005	0.005	100.0
0.010	0.010	100.0
0.020	0.023	115.0
0.030	0.028	93.5
0.040	0.041	102.5
0.050	0.050	100.0
0.060	0.060	100.0
0.070	0.070	100.0
0.080	0.085	102.5
0.100	0.100	100.0

Table 3

Determination of Redistilled Resorcinol

Taken (mg)	Found (mg)	Found (%)
0.000	0.000	-
0.005	0.005	100.0
0.010	0.010	100.0
0.020	0.025	125.0
0.030	0.030	100.0
0.040	0.040	100.0
0.050	0.050	100.0
0.060	0.057	95.0
0.070	0.067	95.7
0.080	0.075	93.5

Table 4

Determination of Resorcinol Containing Impurities

Taken (mg)	Found (mg)	Found (%)
0.000	0.000	-
0.005	0.005	100.0
0.020	0.018	90.0
0.040	0.040	100.0
0.060	0.055	91.7
0.070	0.065	92.7

Table 5

Determination of Recrystallized Pyrocatechol

Taken (mg)	Found (mg)	Found (%)
0.00	0.00	-
0.02	0.02	100.0
0.04	0.04	100.0
0.06	0.065	108.5
0.08	0.07	87.5
0.10	0.11	110.0
0.12	0.11	91.5
0.14	0.13	93.0
0.16	0.15	94.0
0.18	0.18	100.0

To elucidate the effect of impurities, we made experiments on the determination of the resorcinol content in samples containing small quantities of impurities. As these were relatively small we analyzed the preparations, using a standard series from redistilled resorcinol. Our experiments showed the possibility of determining by this means the content of resorcinol in the presence of small quantities of impurities.

We checked the applicability of the method for determining resorcinol in quantities of the order of a few milligrams. For this purpose a weighed quantity

of resorcinol was dissolved in water, an aliquot of the solution was taken and diluted with water so that the color of the reaction product could be determined with the aid of the standard series. We calculated the result of the analysis on the whole volume of solution. Simultaneously, for control, the resorcinol content was checked by the luminescence method. The results of the experiments are set out below:

Taken (in mg)	1.61	2.40	12.0	18.0
Found (in mg)				
Colorimetrically	1.75	2.50	11.0	18.0
Luminescence method	1.70	2.40	11.0	17.6

Determination of pyrocatechol. In Table 5 the results of the determination of recrystallized pyrocatechol are presented.

SUMMARY

A colorimetric method of determining small quantities of dihydric phenols has been worked out for hydroquinone, resorcinol and pyrocatechol, consisting in the action of an ammoniacal solution of cadmium sulfate on the solution of the dihydric phenol and the determination of the quantity of the latter from the intensity of the color of the compound formed.

LITERATURE CITED

[1] N. N. Bovorozhtsov, Fundamentals of the Synthesis of Intermediate Products and Dyestuffs. 2nd Edn. Moscow-Leningrad 264 (1940).

[2] R. P. Lastovsky, Technical Analysis in the Production of Intermediates. Moscow. 194 (1949).

[3] S. M. A. Whetten, Analyst, 74, 185 (1949).

[4] A. L. Kursanov and M. N. Zaprometov, Bio. Chem. 14, 467 (1949).

[5] Ligor Bey, Bull., 51, 230 (1932).

[6] A. G. Stromberg and I. E. Bykov, J. Gen. Chem., 19, 245 (1949).[1)]

Received December 25, 1950.

[1)] See Consultants Bureau English Translation, p. 209.

CONDENSATION OF MENTHONE WITH FORMALDEHYDE[1)]

M. M. Tilichenko and I. A. Evdokimova

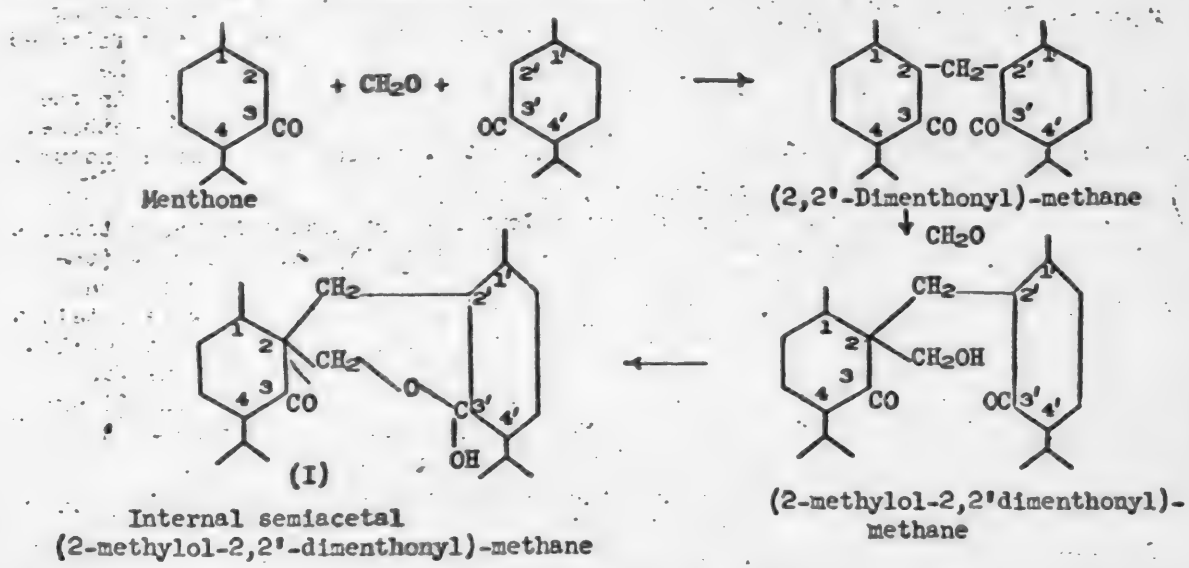
N. G. Chernyshevsky Laboratory of Organic Chemistry,
Saratov State University

Attempts, by Mannich and Brose [1], to condense menthone with formaldehyde (in the presence of calcium oxide) ended in failure: menthone did not enter into reaction with formaldehyde. These authors came to the conclusion that menthone either is completely unable to condense with formaldehyde, or the reaction did not proceed because suitable conditions were not selected.

Somewhat later it was shown [2] that, in the presence of dimethylamine hydrochloride, formaldehyde condenses with menthone in the same way as with other ketones, namely with the formation of α-keto bases. However, the question of the possibility of condensing menthone with formaldehyde in the presence of inorganic bases still remains unsettled.

Since it has not been possible to condense other ketones of this type (carvone, camphone) with formaldehyde [1], the impression has been created that these terpene ketones are in some way set apart in the series of cyclohexanone homologs (cyclohexanone and its simpler homologs very easily condense with formaldehyde [1]).

By condensing menthone with formaldehyde in the presence of 0.3 N alcoholic caustic soda, by the methods worked out in our laboratory, we succeeded in obtaining a condensation product in yield of 32.96% of theory, which, according to the analytic data, is an internal semiacetal, monomethyloldimenthonylmethane. Its formation may be represented as follows:



1) Communication III of a series dealing with the condensation of formaldehyde with ketones and aldehydes.

The condensation may involve the other α-positions and thus, besides the 2-(2,2') it is possible that other isomers of the following form may be produced:

Semiacetal Rings

(II) 4-(2,2')	8-membered
(III) 2-(4,4')	8-membered
(IV) 2-(2,4')	6-membered
(V) 2'(2,4')	8-membered
(VI) 4-(2,4')	8-membered

Of the 6 possible isomeric forms, only I and IV have a 6 membered semiacetal ring (tetrahydropyrane), the other four should be 8-membered. The formation of such 8-membered rings is not excluded but it is less probable than the formation of 6-membered rings.

EXPERIMENTAL

Method of conducting the experiments. To a solution of menthone (1:2.5 M, b.p. 204-210°) in 0.3 N alcoholic NaOH (0.1 M) with constant and energetic mechanical stirring 28.26% formalin[1] (1 M CH_2O) was added slowly, in drops. The bath temperature was 50-70°.

After adding 0.5-0.7 ml of formalin the addition of the latter was interrupted and a Rimini test was made [3]. The feed of formalin was renewed only when the test for free formaldehyde in the reaction mixture was negative.

To terminate the experiment the reaction mixture was diluted with an equal quantity of water and was quantitatively neutralized with 0.1 N sulfuric acid. From the data of titration, the quantity of formaldehyde entering into the Cannizzaro-Tishchenko reaction was calculated, and in this way it was established that the main quantity of the free formaldehyde which disappeared by reaction was consumed in condensing with the ketone. (In the first experiment 14.4% of the formaldehyde, and in the second 12.06% followed the Cannizzaro-Tishchenko reaction).

The upper neutralized mixture of thick oil was separated in a separating funnel, dried with freshly heated sodium sulfate and, after drying, was filtered through a dry filter into a Claissen flask; the unreacted menthone and the volatile part of the condensate was distilled off at 7 mm. The residue in the flask, a glycerine-like syrup with a color of tea and a weak smell of menthone, was subjected to further investigation in order to find out its chemical nature.

Experiment 1. Equimolecular quantities of menthone and formaldehyde were condensed at 50°. In taking successive portions for the Rimini formalin test, a weak positive test was obtained even after 10 hours heating and stirring (the coloration corresponded to that obtained with 0.0001% formaldehyde solution): from 15.4 g of menthone and 10.7 ml of formalin, 17.0 g of dry oil were obtained. Distillation at 7 mm was continued until no more material came over; at 84-118° 8.5 g of a mobile, somewhat yellow liquid with a weak smell of menthone was obtained. 7.1 g of a glycerine-like, tea-colored syrup remained in the flask; it had an average molecular weight of 309.8 and contained 1.55% of OH group (Werle).

The last two values indicate that the OH-containing substance is only an impurity in the syrup. To separate this impurity would not be an easy task (particularly in view of the quantity of substance) and therefore this product was not investigated further.

[1] The formalin was prepared from formaldehyde by heating the latter in water to which a drop of concentrated sulfuric acid was added.

Experiment 2. 1 mole of formaldehyde was mixed with 2.5 moles of menthone. The object of this experiment was to direct the reaction quantitatively towards the formation of the dimenthonylmethane, postulated by us.

For reaction, 24.08 g of menthone and 6.7 ml of formalin were taken. The experiment was conducted at 70° and continued for 2 hours 20 minutes. Five minutes after introducing the last 0.5 ml of formalin, a Rimini test did not disclose any free formaldehyde in the reaction mixture.

22.64 g of a dry oil was obtained, which was vacuum-distilled at 7 mm until distillation ceased.

At 80-90° . . . . . 14.24 g was collected
At 90-117° . . . . . 4.01 g was collected
Residue . . . . . 3.20 g.

The first fraction was a colorless mobile liquid with an odor of menthone and, at ordinary pressure, boiled almost completely at 204-212°, i.e. it was unchanged menthone.

The second fraction was a somewhat yellow mobile liquid with a smell of menthone.

The residue was a transparent, glycerine-like liquid with a color of tea. The results of its further investigation are:

Analysis of the condensate obtained

0.1604 g substance: 0.4418 g CO_2; 0.1608 g H_2O.
0.1464 g substance: 0.4054 g CO_2; 0.1452 g H_2O.
Found %: C 75.16, 75.56; H 11.29, 11.09.
$C_{22}H_{38}O_3$. Calculated %: C 75.48; H 10.86.

Determination of molecular weight

0.1034 g substance; 16.355 g C_6H_6: Δt 0.095°.
0.2042 g substance; 14.921 g C_6H_6: Δt 0.205°.
Found: M 348.6, 349.7.
$C_{22}H_{38}O_3$. Calculated: M 350.

Determination of OH group content

1) By Werle's method:

0.1150 g substance: 5 ml acetylating mixture
0.1002 g substance: 5 ml acetylating mixture
Consumed in back titration with 0.5 N. NaOH:
Control mixture: 29.70, 29.60 ml.
Experimental mixture: 29.80, 29.65 ml.

No hydroxyl group was found.

2) By the Terentyev method [4]:

0.0522 g substance: CH_4 3.7 ml (22°C, 752 mm).
0.0630 g substance: CH_4 4.1 ml (23°C, 751.5 mm).
Found %: OH 4.82, 4.40.
$C_{22}H_{38}O_3$. Calculated %: OH 4.86.

Thus, the experimental data found is in complete agreement with the postulation of a semiacetal monomethylolidimenthonylmethane.

SUMMARY

1. It has been shown that, in alcoholic solutions, in the presence of small quantities of sodium hydroxide, menthone condenses fairly easily with formaldehyde.

2. The condensation product isolated corresponds in composition to an internal semiacetal, monomethyloldimenthonylmethane.

The most probable scheme for the formation of this substance has been given, differing from the known scheme of Tollens, which explains the mechanism of condensation of formaldehyde with monoketones (and aldehydes).

LITERATURE CITED

[1] C. Mannich and W. Brase, Ber., 56, 833 (1923).

[2] C. Mannich and Ph. Honig, C. 1, 202 (1928).

[3] G. Meyer. Analysis and Determination of Organic Compounds, 53, (1937).

[4] Gatterman-Wieland. Practical Work in Organic Chemistry. 96 (1948).

Received July 4, 1950.

HIGH-BOILING IMPURITIES IN VINYL ACETATE

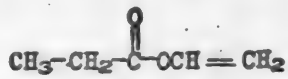
V. I. Lyubomulov, M. S. Akutin, I. V. Chelyshev and S. F. Kalinkin

In crude vinyl acetate, obtained by a vapor phase process, Ushakov and co-workers [1] noted the presence of impurities, boiling approximately 20° higher than vinyl acetate. The fraction separated with b.p. 92-94°, on addition to pure vinyl acetate, caused the latter to polymerize.

In the rectification of crude vinyl acetate, obtained by synthesis under analogous conditions, we also devoted our attention to the high-boiling fractions. At the end of the rectification a fraction was separated with b.p of 94°.

The quantity of high boiling fraction, in relation to the vinyl acetate both in the different syntheses (carried out under approximately identical conditions) as well as in tests taken at different times during the course of one synthesis, varied within wide limits. Sometimes the quantity of high boiling fraction was as much as 10% of the vinyl acetate obtained.

By careful rectification of the high boiling fraction, a substance with a b.p. of 94.5° was separated. The results of analysis showed that this substance was an unsaturated ester, $C_5H_8O_2$. On hydrolysis, propionic acid and acetaldehyde were obtained. This indicates that its structure must correspond to that of the vinyl ester of propionic acid:



The dibromide of this ester was obtained, i.e. the ester of 1,2-dibromoethanol and propionic acid.

EXPERIMENTAL

The synthesis of vinyl acetate was carried out under the conditions described by Ushakov, Rostovsky and Arbuzov [2].

As a support for the catalyst (zinc acetate) different brands of activated carbon were used. The contact tube was of aluminum, heated in an oil bath. The temperature at the beginning of the synthesis was 180° but, as the activity of the catalyst diminished, it was gradually raised to 230°. The acetic acid was of foodstuff quality (State Standard NKLes 235). The products were absorbed by xylene.

The products of synthesis were separated from xylene in a packed column, in which process crude vinyl acetate was withdrawn as the fraction boiling up to 118°. From this raw material a fraction of vinyl acetate was distilled off up to a temperature of 75.5° in the fractionating column. The residue in the flask was transferred to an aluminum flask and subjected to a number of careful successive rectifications in a column of height 1.2 m packed with glass Raschig rings 7 x 7.

A colorless liquid with an odor reminiscent of pear oil, whose b.p. did not change on successive rectifications, was separated.

B.p. 94.5° (760 mm); n_D^{20} 1.4061; d_4^{20} 0.9121.

Found: MR 26.96.
$C_5H_8O_2$. Calculated : MR 26.48.
0.1103 g substance: 0.2421 g CO_2; 0.0831 g H_2O.
Found %: C 59.91; H 8.37.
$C_5H_8O_2$. Calculated %: C 59.96; H 8.06.
0.1200 g substance: 20.0 g benzene; $\Delta t = 0.310$.
Found: M 98.7
$C_5H_8O_2$. Calculated: M 100.06.

Determination of bromine number (Kauffmann)

0.1072 g substance: 19.7 ml 0.1 N hyposulfite (difference)
Found bromine no: 1473
$C_5H_8O_2$. Calculated bromine no: 1597

The determination of the bromine number by this method usually gave a low result on pure vinyl acetate also.

Determination of the saponification number (at room temperature):

0.4802 g substance: 9.60 N ml NaOH (0.5 N).
Found: Saponification number 558.

$CH_3CH_2-\overset{\overset{O}{\|}}{C}-O-CH=CH_2$. Saponification number calculated 560.

The ester was hydrolyzed with 0.5 N sulfuric acid at the boil in a flask equipped with a stirrer. The vapor was led through a fractionating column and was then condensed in a condenser fed with a cooling mixture. In the flask, the formation of a considerable amount of resin (aldolization) was always observed, as a result of which the yield of aldehyde was extremely small. Thus, with a weight of 20 g of substance and 50 ml of 0.5 N sulfuric acid, 6.5 g of aldehyde fraction distilled off. After drying with calcium chloride the distillate was rectified in a 3-bulb fractionating column and redistilled completely to 29°, a somewhat higher temperature of boiling compared with that of acetaldehyde and caused, apparently, by insufficient drying.

2,4-dinitrophenylhydrazone was obtained by adding 3-4 drops of aldehyde to 0.2 g of 2,4-dinitrophenylhydrazine in alcohol. After heating and subsequent cooling, long yellow-orange needles came down. After recrystallization from alcohol, m.p. 160°, m.p. of the 2,4-dinitrophenylhydrazone of acetaldehyde is 162° [3]. To check this, acetaldehyde was obtained (by hydrolysis of pure vinyl acetate), and from it, in an analogous manner, the 2,4-dinitrophenylhydrazone was obtained with an m.p. of 160.5°. The mixed samples melted at 160.2°.

After the cessation of distillation of the aldehyde during the hydrolysis, the distillation of the acid from the flask was continued, and this was neutralized with caustic soda and the salt solution was evaporated. After acidifying with sulfuric acid, the mixture was extracted with ether. The ethereal extract was dried with calcium chloride and the residue, after distilling off the ether, was rectified in a 3-bulb rectifying column.

B.p. 139-140°; d_4^{20} 0.9827; n_D^{20} 1.3870. For propionic acid, b.p. 140.1°, d_4^{20} 0.9916; n_D^{20} 1.3874 [4].

0.1626 g substance: 22.1 ml 0.1 N NaOH.
$C_5H_8O_2$. Calculated %: 22.0 ml 0.1 N NaOH.

The acid was neutralized with caustic soda (not containing chlorine) and by adding silver nitrate the silver salt was precipitated. It was dried in a dessicator to constant weight.

0.5544 g substance: 0.3306 g Ag (after heating)
Found %: Ag 59.63.
$C_3H_5O_2Ag$. Calculated %: Ag 59.63.

For bromination of the ester, 5 ml of bromine was added in drops to a solution of 11.1 g of vinyl propionate in 50 ml of ether, cooling at the same time. After distilling off the ether 1 g of sodium bicarbonate was added to the residue and the product was distilled under vacuum. The main fraction of 11.4 g boiled (35 mm) at 116-118°; d_4^{20} 1.7377; n_D^{20} 1.4941. It was a colorless oily liquid momentarily going yellow when dust particles fell into it; it did not dissolve in water but dissolved rapidly in 0.1 N NaOH on shaking, as a result of which it was quantitatively saponified. Thus 50.0 ml of 0.1 N NaOH was added to 0.2494 g of 1,2-dibromoethyl propionate. After 15 minutes shaking this quantity had completely dissolved. On back-titration 19.7 ml of 0.1 N HCl was used. 30.3 ml of 0.1 N NaOH had reacted to combine with the propionic acid and 2 moles of hydrobromic acid from bromine in $C_5H_8O_2Br_2$; calculated 28.8 ml of 0.1 N NaOH. After this the contents of the flask were titrated with 0.1 N silver nitrate (Mohr). 39.5 ml of 0.1 N $AgNO_3$ were used up. On titration of 50.0 ml of 0.1 N NaOH, neutralized by nitric acid not containing chlorine, 0.8 ml of silver nitrate were consumed (control experiment to check whether the NaOH was contaminated with halide). Thus the weighed sample combined with an amount of bromine equivalent to 19.0 ml of 0.1 N $AgNO_3$. The calculated figure is 18.8.

The polymerization of vinyl propionate was carried out under the conditions under which vinyl acetate is usually polymerized, i.e. by heating with 0.2% of benzoyl peroxide on a water bath with or without solvent; it did not polymerize during 5 hours. However it polymerized on standing for a few months in a test tube at room temperature in the presence of benzoyl peroxide. A viscous (almost solid), colorless, transparent polymer was formed.

The propionic acid in the acetic acid, used for the synthesis of vinyl acetate, was determined by the bromate method [5]. The propionic acid content found was 1.1%.

SUMMARY

It has been established that the high boiling impurities in vinyl acetate obtained by vapor phase syntheses, arevinyl propionate.

LITERATURE CITED

[1] S. N. Ushakov, I. F. Markov, D. I Manevich and I. A. Broitman, Ind. Org. Chem. 8, 445 (1940).

[2] S. N. Ushakov, E. N. Rostovsky, I.A. Arbuzov, J. Appl. Chem. 13, 11, 1629 (1940).

[3] G. Meyer, Analysis and determination of organic compounds, 58 (1937).

[4] Beil. H., 2, 235-236; 2 Erganzungsband, 102.

[5] F. Baum. Chem. Z. 51, 54, 517 (1927).

Received July 20, 1948.

BLANK
PAGE

BOOK REVIEW

B. N. Dolgov, Catalysis in Organic Chemistry (State Chem. Press, Leningrad-Moscow, 1949, 560 pp. Authorized by the Ministry of Higher Education of the USSR as a textbook for chemical-technical high schools and faculties)

At present there is an acute need for a textbook and monograph on catalysis in general, and catalysis related to organic chemistry in particular; hence, the appearance of this first indigenous treatise on catalysis in organic chemistry should be considered of extreme importance. The vigorous development of contemporary organic chemistry and the whole increase in importance of catalysis in industrial organic synthesis requires that the modern chemical specialist should be well versed in the fundamentals of catalysis and with the applications of catalysis in industry. Moreover there is at present no handbook or text book, devoted to this important topic. The very few monographs and separate works on catalysis which exist belong to the 1930-1937 era, are clearly dated and do not reflect the enormous advances which have been made in catalysis in recent years, especially by Soviet scientists. Thus the need for a manual on catalysis in organic chemistry developed sometime ago, and the work reviewed here is a successful attempt to fill this lacuna.

In spite of the fact that it is described as a text-book by the author, this work will also be found very interesting by scientific workers, since the author has been able to collect new experimental material, excellently illustrated by numerous reactions, and gives the present-day theoretical basis for the phenomena examined. The creation of such a work has presented no light task, in view of the enormous mass of experimental material, a considerable part of which has not yet been brought within the scope of any theory. It must also be borne in mind, that it would be difficult to find in contemporary chemistry another subject which has such a great practical importance as catalysis. Apart from this, catalysis is a typically complex problem and the range of topics, directly or indirectly connected with catlytic reactions, is extremely large. In the field of catalysis, perhaps more acutely than in other branches of chemistry, the struggle of the materialistic point of view with idealistic and one-sided mechanistic interpretations has lasted from the time of Berzelius and Ostwald to our own times, and it still continues. The writer of a book on catalysis cannot pass this question by, and it finds its reflection to a greater or lesser degree in the work under review.

The book has the main merit that the extremely varied material included within its covers is brought within a strict classification and thanks to this the exposition is extremely clear and consistent. This presentation of an enormous mass of material in very compact form, (in parts practically concrete) is given in so masterly a fashion, that the reader is not exhausted but instead reads this original work with enthusiasm. Another important point is the wide and understanding use made of the work of Russian and Soviet scientists, who have made a large contribution to the development of this important field of organic chemistry. The successful execution of the difficult task of writing an original manual on catalysis in organic chemistry is conditioned by the fact that Prof. B. N. Dolgov is an investigator of great stature in the field, with a large knowledge of industrial organic syntheses. His brilliant erudition and great instructional skill find their reflection in the pages of this book. Of course there is no doubt that in the exposition of so large a mass of material, covering almost a hundred-year period, there are some omissions and inaccuracies in the treatment

of individual topics.

The whole book consists of an " introduction" and 11 chapters, which are not equal in size.

In the " Introduction" the history of catalysis in organic chemistry is dealt with briefly, and the leading role of native scientists is emphasized: A. M. Butlerov, A. M. Zaitsev, E. I. Orlov, N. D. Zelinsky, A. E. Favorsky, S. V. Lebedev, B. A. Kazansky and the schools of Soviet chemists which they have created.

In the first chapter the principles and the factors involved in catalytic reactions are expounded. In the section "Principles of Catalysis" the author considers the basic physico-chemical concepts necessary for the understanding of catalytic processes. In the section " Factors of Catalysis", he examines, together with the effects of temperature and pressure, the flow rate, the time of contact, the activity number, quoting formulas for calculation which are extremely important for practical work in the field of catalysis. In his exposition of catalysts the author successfully combines in one chapter both the methods of preparation of different catalysts (precipitated, fused, colloidal) as well as the phenomenon of promotion and of contact poisoning. This section could with advantage be supplemented by a classification of catalysts, with even a short description of their characteristics.

In Chapter II the theory of catalysis is examined, the author devoting most consideration to the adsorption theory. The nature of active centers and their importance for the understanding of the nature of the catalytic activity of substances is gone into, and here the author gives support to Koboser's ensemble theory. Considerable space is set aside for the examination of the theory of activated adsorption. For the explanation of the mechanism of the catalytic reactions on surfaces the author brings in the theory of activated complexes, supplemented by his own multiplet theory. Here it is impossible to agree with the author's representation of the mechanism of certain surface reactions on active centers by means of the doublet and quadruplet mechanism, (pp. 108-110) since this scheme gives only a formal picture of the phenomena without going into the physical background.

In Chapter III catalytic oxidation is examined in fair detail (69 pp). The great variety of oxidation reactions is classed by the author as follows: 1) oxidation (complete and incomplete); 2) destructive oxidation; and 3) self oxidation. Examining the cases of complete oxidation, the author notes that up to the present insufficient attention has been paid to these reactions and only the present-day development of surface and air transport, requiring specially-prepared fuels, has given a special importance to the question of the complete combustion of hydrocarbons and their mixtures. In the section on destructive oxidation the author devotes special attention to the work on the gasification of solid fuel (underground gasification of coal and shale), indicating that this idea was first put forward by D. I. Mendeleev in 1888, and was first realized in the USSR in 1938. In this chapter there is a fairly complete exposition of the current theoretical concepts about the processes of oxidation (A. Bach's peroxide theory, chain mechanism theory of Semenov and his school, etc.).

In Chapter IV the processes of dehydrogenation are described. The classical investigations of N. D. Zelinsky and his school on the aromatization of the polymethylene hydrocarbons is noted. In the section on dehydroxylation the work of Moldavsky and his school is examined, and that of Kazansky and Platt on the conversion of aliphatic to aromatic hydrocarbons. The original work of Soviet scientists on dehydrogenation condensation of esters and ketonization of alcohols is also examined, work which is of great interest, but which, unfortunately, the author presents in a very brief and compressed form.

In Chapter V catalytic cracking is examined.

The most bulky chapter is the sixth one, devoted to hydrogenation (96 pp). The author classifies catalytic reactions with hydrogen as follows: 1) catalytic hydrogenation or addition of hydrogen at unsaturated bonds; 2) catalytic reduction, addition of hydrogen to oxygenated groups; 3) destructive hydrogenation (hydrogenolysis); and 4) the catalytic redistribution of hydrogen, or dehydrogenation. Hydrogenation under high pressure is described, the author demonstrating that the first autoclave was constructed in Russia and thereby created a new era in the scope of chemical reactions. The author also mentions that hydrogenation in vacuum was first accomplished by N. D. Zelinsky. In this chapter there is a fairly complete examination of the works of the following Soviet scientists: N. D. Zelinsky, S. V. Lebedev, S. S. Nametkin, B. A. Kazansky, A. D. Petrov, V. V. Ipatiev, A. I. Yakubchik, L. I. Antsus and others.

In the examination of the hydrogenation of the benzene ring, (p. 261), and also of the reduction of acids to alcohols (pp. 302-303) the author uses the formal schemes of the theory of resonance in order to explain the sluggishness of these processes, and it is impossible to agree with this. In the section on destructive hydrogenation the author, describing the process of hydrogenation of coal, preserves for the process the term "berginization" (pp 312) which is scarcely desirable. The chapter closes with an exposition of the theory of hydrogenation.

In Chapter VII catalytic dehydration is described. The reactions involved here are subdivided into intramolecular and intermolecular dehydration, to the latter belonging hetero- and homo-condensation and condensation polymerization. In this chapter the reactions involved in the preparation of ethers and esters, dialcohols, dienes, (butadiene, ketene); the dehydration of glycols and acids, and the pinacoline rearrangement are discussed. Considerable space is devoted to the preparation and properties of plastics, (alkyd, phenol- and urea-formaldehyde resins, casein plastics, polyamide fibers). It would be an advantage to bring in at this point the description of thiokol, which is actually delayed to Chapter XI.

In Chapter VIII catalytic hydration is examined, including hydrolysis and alcoholysis. The author brings in a number of interesting pieces of work by Soviet scientists: the preparation of phenol from chlorobenzene (D. V. Tishchenko, N. N. Vorozhtsov, Jr., and co-workers), the contact saponification of fats (Petrov), the hydrolysis of albumens (Sadikov, Zelinsky, Gavrilov). Alcoholysis could with advantage be extended to include the reactions involved in the per-esterification of methyl methacrylate, used for obtaining the higher esters of methacrylic acid.

Chapter IX is devoted to polymerization and copolymerization. The author shows quite convincingly the priority of Russian chemists in the field of polymerization of unsaturated compounds (A. M. Butlerov, I. L. Kondakov), and the preparation of synthetic rubber (I. I. Ostromyslensky, S. V. Lebedev, B. V. Byzov, A. E. Favorsky). He describes the main kinds of industrial polymers and copolymers. Since this field of organic chemistry is in a state of very rapid growth, the material in this section, particularly in the part dealing with the mechanisms of polymerization and copolymerization, is quite clearly insufficient and should be considerably extended in later editions.

In Chapter X syntheses based on carbon monoxide are dealt with. Here the methods are expounded of synthesizing liquid fuels, methanol, and higher alcohols, which were to a considerable extent worked out by the author of the book himself and his coworkers, and the method of transferring these reactions from the laboratory to the industrial scale is demonstrated.

Chapter XI is devoted to catalytic halogenization. In the examination of the electronic mechanisms of some cases of halogenization, the author treats the addition of bromine to butadiene (p 533) according to the older and incorrect resonance theory.

From all this survey it follows that the observations we have made in no wise detract from the value of the book, which is the first native-produced manual on catalysis in organic chemistry. It may confidently be expected that in future editions (for which there will be a definite need) the author will, after working over certain sections, present a still more complete picture of the current state of development of catalysis in organic chemistry.

M. M. Koton

E ROLE OF COMPLEX
ILVER COMPOUNDS IN
TOGRAPHIC DEVEL-
ENT, p. 1295.

Fig. 5. Microphotograph of transverse section through the layer.

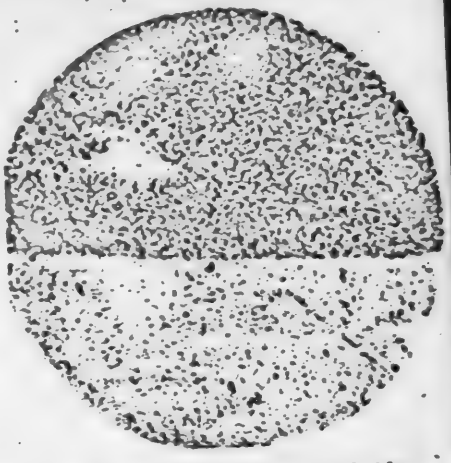
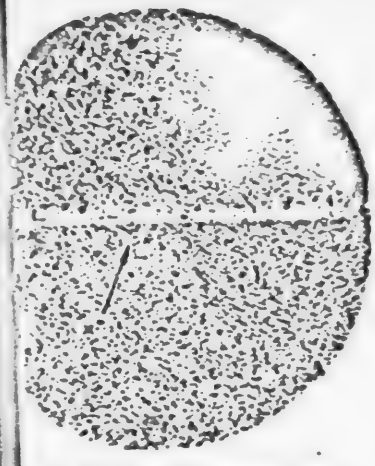


Fig. 8. Microphotograph of the edge of the image in contact with AgBr.



. 9. Microphotograph of edges of the image after contact with AgBr.

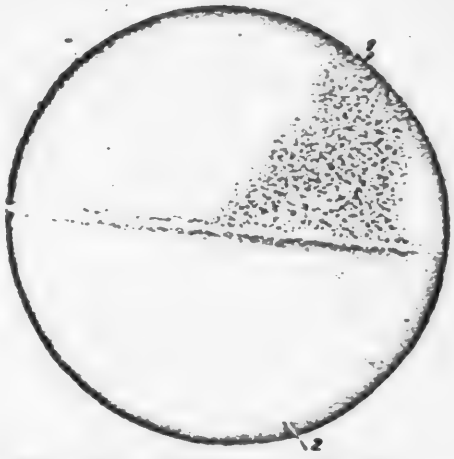


Fig. 10. Effect of the adjacent region with addition of $Na_2S_2O_3$.

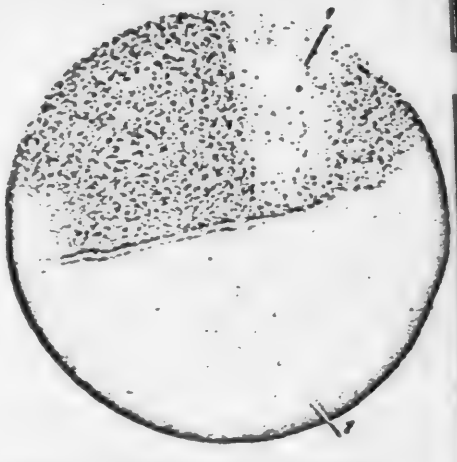


Fig. 11 Effect of adjacent region without addition of $Na_2S_2O_3$.
1) Primary image; 2) secondary image.

CORROSION OF IRON BY BENZENE SOLUTIONS OF IODINE, p. 1301.

a b

Fig. 2. a) X-Radiogram from the deposits obtained;
b) X-Radiogram from pure Kahlbaum ferric oxide.

BLANK
PAGE